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LABORATORY ASSESSMENT OF POTENTIAL HYDROCARBON EMISSIONS FROM LAND TREATMENT OF REFINERY OILY SLUDGES

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by

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16. ABSTRACT

Volatile organics emissions were characterized when petroleum refinery oily sludges were incorporated in soils under controlled laboratory conditions. The sludges tested included three of the five listed hazardous wastes for the refining industry: dissolved air flotation float, slop oil emulsion solids, and API separator sludge. The volatile components of the sludges were first identified. Then the effects of the following operating conditions on volatile emissions were studied: air temperature and humidity, wind speed, soil type, temperature and moisture, sludge loading and volatility, and method of waste application. The volatile components identified in the sludge were also present in the emissions from the soil-waste mixtures. The quantity of emissions were most affected by the sludge volatility, sludge loading, application method, and atmospheric humidity, and the cumulative emissions at a given period of time could be correlated with these operational variables. The emission rate or level was not significantly affected by soil type or soil moisture. An expression for estimating the rate of emissions as a function of elapsed time after application could not be developed from the data. While every effort was made to simulate actual land treatment conditions, it is not possible to directly apply these laboratory findings to predict full-scale results.

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FOREWORD

The Environmental Protection Agency is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life. In partial response to these mandates, the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, is charged with the mission to manage research programs to investigate the nature, transport, fate, and management of pollutants in ground water and to develop and demonstrate technologies for treating wastewaters with soils and other natural systems; for controlling pollution from irrigated crop and animal production agricultural activities; and for developing and demonstrating cost-effective land treatment systems for the environmentally safe disposal of solid and hazardous wastes.

There has been increasing interest in the organics losses through volatilization when refinery oily wastes are applied to and incorporated into land treatment soils. This interest was the basis for this study, which represents a laboratory simulation to characterize the air emissions and determine the relative effects of operational parameters in land treatment of refinery sludges.

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SECTION 1

INTRODUCTION

The landtreatment of oily refinery sludges has become an important method for disposing of this waste material. In recent years, there has been an increasing interest in defining the presence and magnitude of volatile organic compound (VOC) emissions from the landtreatment of organic wastes. Radian Corporation has performed a laboratory study to assess the atmospheric emissions from the landtreatment of refinery sludges. Both the magnitude of emissions and the significant variables affecting the emissions have been investigated. This program was jointly funded by the American Petroleum Institute (API) and the Environmental Protection Agency (EPA).

Two phases of this program have been completed. In phase I, completed in early 1981, a small number of refinery sludge and landfarm soil samples were obtained from cooperating refineries. These were characterized by physical and chemical testing. A laboratory landtreatment simulation apparatus was developed and landtreatment simulation experiments were performed with the refinery soil and sludge samples. Emissions from these simulations were measured, and some of the potentially important parameters affecting these emissions were tentatively identified.

Phase II of this study was performed to provide a more comprehensive characterization of refinery sludges and landfarm soils and to evaluate the effects of operating and process variables on the VOC emission levels. Nine refinery sludges and eight landfarm soils were collected and characterized. The laboratory simulation apparatus was modified to provide additional data and automated data collection. Over forty successful simulation test runs were performed.

The results of phase II of the landtreatment study are presented in this report. Where appropriate, results obtained during phase I of the study are included to provide additional helpful information. The conclusions drawn from the results of this study are included in Section 2 of the report. Section 3 contains descriptions of the experimental procedures which were used in this program. The quality control/quality assurance (QA/QC) procedures and results are also included in Section 3.

The results of the phase II activities are presented and discussed in Sections 4 and 5, respectively. Finally, recommendations regarding further research needs and the sequence of these activities is provided in Section 6. Some additional detailed information and data are provided in the Appendices.

SECTION 2

CONCLUSIONS

The phenomena associated with the emissions of volatile organic compounds (VOC) and other gaseous compounds from the land treatment of refinery oily sludges are extremely complex. For this reason both the Phase I and Phase II studies have been limited in their scope and have concentrated primarily on a broad evaluation of the emissions process.

In Phase II the effects of sludge volatility, soil loading, soil type, soil moisture, and air himidity on landfarm VOC emissions were studied. The effects of air temperature, soil temperature, wind speed, and biodegradation were not studied in the Phase II program. It appeared from the Phase I results that wind speed did not affect the emissions level.

The subsurface injection of sludges was also not studied in Phase II. The results obtained during Phase I indicated that the emissions from this type of application were negligible at least within the first hour after application. The sludges studied in Phase II were much less volatile than those of Phase I. As a result, it was felt that the emission level from subsurface application would not be measurable with the available test apparatus. An even more sensitive hydrocarbon detection method will probably be needed to study the emissions from subsurface injection.

The results of work performed as part of Phase II work indicate that for tests using the laboratory landfarm simulation apparatus:

- The volatile components identfied in the sludge were also present in the emissions from the land treatment of the sludges. The lighter (more volatile) compounds were present in the emissions at relatively higher concentrations compared to their concentrations in the sludge.

- The level of emissions is affected by the sludge volatility, the sludge loading, and the atmospheric humidity.
- The cumulative emissions at a given period in time (four to seven hours after application) can be correlated with the sludge volatility, the sludge loading, and the atmospheric humidity.
- The emission rate or level is not significantly affected by the type of soil or its moisture content.
- An expression for estimating the rate of emissions as a function of elapsed time after sludge application could not be developed from the available data.

It is important to note that test results were obtained in a laboratory. While every effort was made to simulate actual landfarm conditions, it is not possible to directly apply these test results to the case of a full-scale operating landfarm.

Relative to analytical techniques and procedures, the following was also learned:

- The sludge stripping test used in this study appears to be a valid method of estimating relative sludge volatilities.
- The estimation of the oil content of the sludge by Freon extraction, using either gravimetric or IR techniques, is inappropriate for oily wastes.
- Sample preservation through refrigeration and aliquoting is essential to maintaining the sample's chemical integrity.

SECTION 3

EXPERIMENTAL APPROACH

The experimental portion of this project had four major objectives. These were to:

- Obtain detailed information and samples of sludge and soil from several refineries that employ landtreatment of sludges;
- Characterize the sludge and soil samples for their chemical and physical nature;
- Choose representative sludge and soil samples to cover a broad range of conditions typical of the landtreatment process;
- Use the selected representative sludge and soil samples for laboratory controlled landtreatment simulation experiments to evaluate the potential hydrocarbon emissions.

The work done in each of these areas is described in the following subsections.

3.1 INFORMATION AND SAMPLE ACQUISITION

With the aid of the API committee on landtreatment, a questionnaire was developed to obtain information from candidate refineries. A blank copy is contained in Appendix A. It consist of four parts:

Introduction--

The introduction was designed to provide background information to the refinery. It served as written confirmation of a request for cooperation in the project.

General Questions--

This section was designed to provide identification of the refinery and some details concerning sludge production rates and composition. Sampling and shipping requirements were also included.

Soil Sample--

Historical details covering the landtreatment area and the particular sampled soil were requested in this section.

Sludge Sample--

Details concerning origin and history of the sludge sample were requested.

Eight refineries participated in this study. They provided eight soil samples and nine sludges for testing. The soils were designated D-1 through D-8 and the corresponding sludges were designated SL-11 through SL-19.

Each soil and sludge sample was analyzed for several chemical and physical characteristics. Large quantities of three soils representing the spectrum of observed types were then obtained to perform the simulation experiments.

3.2 SOIL CHARACTERIZATION

Soil samples from the participating refineries were subjected to characterization tests to determine the following:

- pH
- specific gravity
- moisture
- particle size distribution
- classification (sand, silt, clay)
- oil and grease

- organic carbon by heating
- organic carbon by titration (oxidizable carbon)

A brief description of each test follows.

pH (Agriculture Handbook, No. 60, Method 21)--

A slurry of 10 grams of distilled water and 5 grams of soil was shaken for 1 hour. The pH was then measured and recorded.

Specific Gravity (ASTM D854-54)--

The volume of an accurately weighed dry soil sample was determined by hexane displacement. The weight of hexane added to a 100 ml container of soil was determined. The volume of the added hexane was subtracted from the total volume (100 ml) to determine the soil volume.

Moisture Content--

The weight loss after heating a soil sample to 50°C (122°F) for 16 hours was attributed to moisture. This method deviates from the standard test for moisture in which a temperature of 105°C is maintained. The lower temperature procedure has been successfully used by Radian to reduce the volatilization of organic materials in solid wastes.

Particle Size Distribution (ASTM D422)--

This test consisted of a standard sieve analysis with screen openings ranging from 75 to 4750 microns in diameter. A hydrometer test was used to determine particle sizes in the range between 1 and 75 microns.

Classification (ASTM D2487)--

The particle size distribution data for each soil was evaluated for relative abundance in certain ranges. Adherence to the gradations commonly used by soil scientists provided a classification of each soil as sand, silt, clay, or a combination of two types.

Oil and Grease Content (EPA Method 413.1)--

The organic material extracted from a soil sample with Freon was considered its oil and grease content. The amount extracted was determined by evaporating the Freon and weighing the residue.

Organic Carbon by Heating (ASTM D2974)--

Dried soil samples were heated to 500°C for eight hours. The weight lost was attributed to organic carbon.

Organic Carbon (Oxidizable) by Titration--[1]

Each soil sample was heated and allowed to react with a known quantity of $K_2Cr_2O_7$. Unreacted dichromate was titrated with a standardized $FeSO_4$ solution. The dichromate was assumed to react (oxidize) any organic material present in the soil. Any material other than carbon that is contained in the soil sample could also be oxidized by $K_2Cr_2O_7$ under the test conditions. Such additional oxidation would obviously introduce some error into the results.

The results of these tests are presented in Section 4.

3.3 SLUDGE CHARACTERIZATION

Sludge samples from the participating refineries were subjected to characterization tests to determine the following:

- volume of oil, water, and solids (by centrifugation);
- oil and grease content;
- chemical composition; and
- volatility.

Brief descriptions of these tests are presented below.

Centrifugation--

A two hundred milliliter sample of sludge was centrifuged for 5 minutes at 5000 rpm. In most cases, three distinct layers were obtained. The top layer was oil; the middle layer was water, and the bottom layer was solids. The volume of each layer was determined.

Oil and Grease (EPA Methods 413.1 and 413.2)--

Both procedures utilize a Freon extraction of the oil and grease from the sludge. In the gravimetric procedure (413.1) the Freon is distilled off and the residue (considered to be oil and grease) weighed. In the IR method (413.2), the relative absorbance of the C-H stretch band is measured, and the organic concentration calculated from Beer's Law. Calibration is effected by determining the extinction coefficient of a reference oil containing 37.5% isooctane, 37.5% hexadecane, and 25% benzene.

Chemical Composition--

The chemical composition of each sludge was determined by gas chromatography/mass spectrometry. One gram of sludge was extracted with 10 milliliters of methanol. Internal standards of d_8-toluene and d_{10}-anthracene were added to a 1 ml aliquot of the extract. Quantitation was only performed for the largest peaks.

Volatility--

A volatility or stripping test was developed by Radian during phase I of this project. The experimental apparatus employed in phase II was almost identical to that used in phase I. A schematic diagram is shown in Figure 3-1. Notable changes are given below.

1) A Byron Model 401 Total Hydrocarbon (THC) analyzer was used in place of the Byron Model 301 analyzer. After injection, the entire sample is swept into a flame ionization detector. The analytical cycle time is reduced to 1 minute from the 4 minute cycle of the 301.

2) The N_2 purge rate was increased to 200 cc per minute from the 100 cc per minute in phase I.

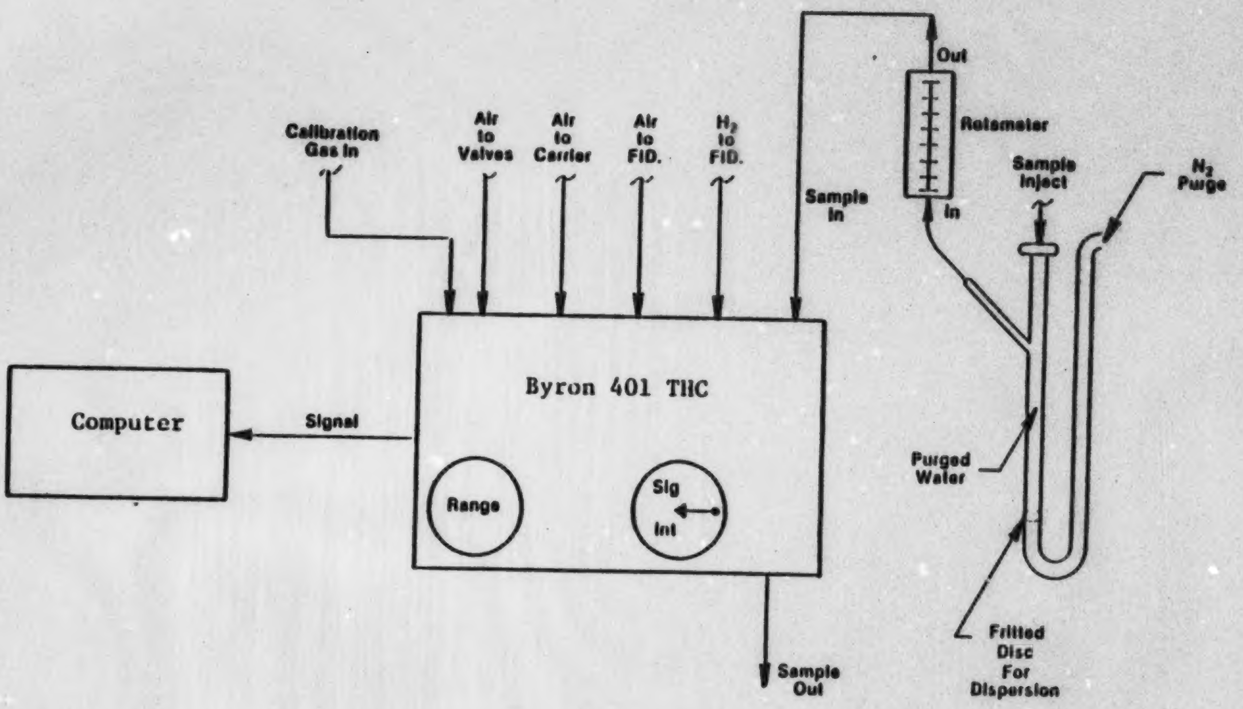

Calibration Gas In
Air to Valves
Air to Carrier
Air to FID.
H_2 to FID.
Sample In
Out
Rotameter
In
Sample Inject
N_2 Purge
Byron 401 THC
Computer
Signal
Range
Sig
Int
Purged Water
Sample Out
Fritted Disc For Dispersion

Figure 3-1. Stripping Test Apparatus

3) Calibration of the Byron 401 was performed with certified standard gas containing hexane in air. This calibration will be discussed further in Section 3.5.

4) Sample exhaust was not collected (since the short cycle time gave accurate curves for integration).

5) The monitoring period was increased from 80 minutes to more than 240 minutes.

6) Integrated area data were collected automatically by a microcomputer-based data acquisition system.

Most of the volatility tests were conducted with 1.0 ml of sludge. This was 20 to 100 times the amount of sample used in Phase I and is an indication of the much lower volatility of the sludges tested during Phase II.

3.4 SIMULATION EXPERIMENTS

The simulation of actual landtreatment activities and measurement of emissions under laboratory conditions was a major objective in this second phase. At the conclusion of Phase I, several parameters were tentatively identified as impacting the level of VOC emissions from landtreatment. Relatively strict control of some of the parameters required modification of the basic simulation apparatus used in Phase I.

3.4.1 Experimental Design

Of the parameters surveyed in Phase I, five were chosen for intensive study in Phase II. These were:

- sludge volatility,
- soil loading,
- soil type,
- soil moisture, and
- air humidity.

In general, three to five levels of each parameter were considered sufficient to define its contribution to fugitive VOC emission. Due to time and monitoring constraints, a parametric study with strict statistical guidelines was devised. Considerations concerning the five major factors are given below.

Sludge Volatility--

Volatility was found to be almost overwhelming in its effect during phase I. After a review of the stripping test data and composition data for phase II sludges, three were chosen as representing low, medium, and high volatility sludges. These sludges were SL-12, SL-14, and SL-11, respectively. An alternate sludge, SL-13, was chosen as a medium volatility sludge because of the relatively small amount of SL-14 on hand.

Soil or Sludge Loading--

In phase I, the amount of sludge applied to the soil was kept constant without regard to its oil content. In phase II, the oil content was considered in determining the loading rates. Thus, the variable was the amount of oil applied. Five target levels ranging from 0.05 to 2.0 pounds oil per square foot (7 to 190 bbl/acre) of soil were chosen. Experimentally, the very low target values were sometimes difficult to attain, chiefly due to solids adhering to the sample container during application. The high loading rates were difficult with those sludges having low oil contents. The amount of required sludge was often excessive in these cases.

Soil Types--

Review of the classification data for the soil samples resulted in the relatively obvious choices of D-1 as predominately sand, D-8 as predominantly silt, and D-7 as predominantly clay.

Soil Moisture--

The results obtained during phase I indicated a relatively strong dependence of VOC emission rates on the soil moisture. In these phase II experiments, five levels of soil moisture were used. In each case, the soil was heated to drive off water until the level was below the desired value. Just before an experimental run, sufficient water was added to bring the moisture content to the desired level.

Air Humidity--

Relative humidity in phase I was not a controlled parameter. In one experiment, the humidity was raised to the highest attainable level. The results indicated a strong effect of humidity on the VOC emission rate. In phase II, the simulation apparatus was modified as described in Section 3.4.3 to allow control of the air humidity. Three humidity levels were studied.

Other Variables--

The phase I experimental results indicated some effects of soil and air temperature on VOC emissions. These temperatures were controlled and monitored but were not varied, because of the limited scope of the phase II program. A temperature of 90°F was felt to be reasonably representative of the higher ranges of field conditions for both media.

3.4.2 Experimental Matrix

All of the factors described in the previous section were combined with the statistical requirements of a parametric study. The resulting matrix of experimental conditions is given in Table 3-1. The run ID number is a sequential identification number utilized by the data acquisition system. The missing runs (1, 3, 4 etc.) were either performed for quality control purposes, or aborted due to analytical or experimental problems. The results of the successful experiments are given in Section 4 and discussed in Section 5.

3.4.3 Simulation Apparatus

Several improvements and changes in the basic simulation apparatus and analytical measurement devices were made to improve the control capability and the accuracy or precision of the measurements. A schematic of the apparatus is given in Figure 3-2. A description of the modifications is given below.

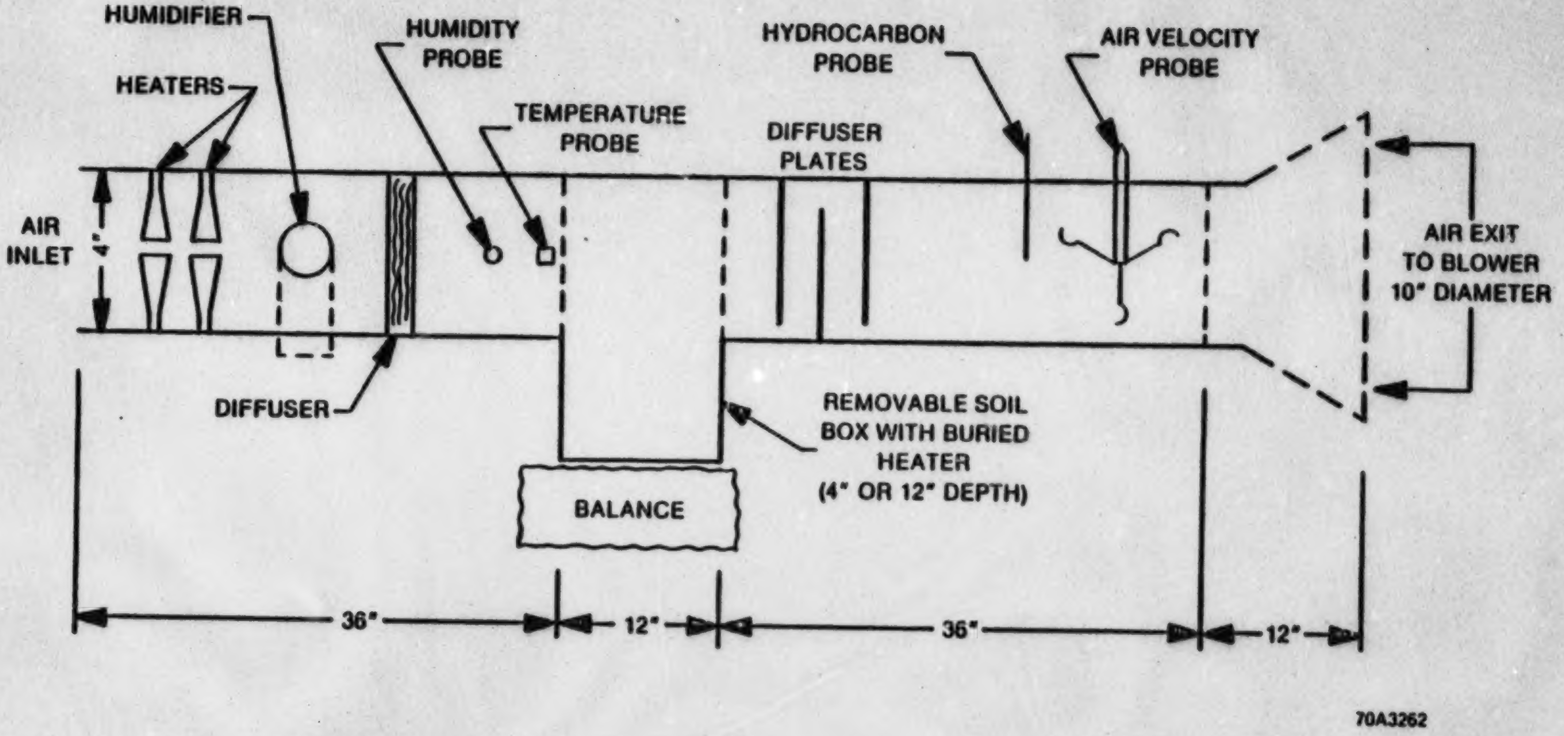
TABLE 3-1. EXPERIMENTAL CONDITIONS FOR LANDTREATMENT SIMULATIONS

Run ID No.	Sludge ID No.	Sludge Loading Lb/Ft^{2b}		Soil ID Number	Soil Moisture Content, Wt. %	Air Relative Humidity %	Temperature °F	
		Total	Oil Only				Soil	Air
2	SL-11	2.0	1.0	D-7	25	50	90	90
5	SL-11	2.0	1.0	D-7	25	50	90	90
6	SL-11	0.6	0.3	D-7	25	40	90	90
7	SL-12	2.1	0.49	D-7	25	50	90	90
8	SL-14	2.1	0.45	D-7	25	50	90	90
9	SL-14	1.5	0.32	D-8	10	50	90	90
10	SL-11	2.1	1.05	D-8	10	50	90	90
11	SL-11	2.0	1.0	D-1	10	50	90	90
12	SL-11	0.6	0.3	D-1	10	50	90	90
13	SL-14	2.3	0.49	D-1	10	50	90	90
15	SL-11	1.0	0.5	D-1	10	50	90	90
16	SL-11	1.0	0.5	D-8	10	50	90	90
17	SL-12	2.13	0.50	D-7	25	50	90	90
18	SL-14	0.467	0.10	D-8	10	50	90	90
19	SL-12	1.06	0.25	D-8	10	50	90	90
20	SL-12	6.4	1.50	D-8	10	50	90	90
21	SL-11	1.0	0.5	D-1	10	30	90	90
22	SL-11	4.0	2.0	D-1	25	30	90	90
24	SL-14	1.5	0.32	D-8	10	50	90	90
25	SL-11	1.5	0.75	D-8	10	30	90	90
26	SL-11	0.1	0.05	D-8	15	70	90	90
27	SL-11	0.1	0.05	D-7	15	70	90	90
29	SL-14	4.65	1.00	D-8	5	70	90	90
29	SL-14	2.13	0.46	D-1	25	30	90	90
32	SL-11	1.17	0.59	D-7	25	50	90	90
33	SL-11	2.34	1.17	D-7	15	70	90	90
34	SL-14	6.0	1.28	D-7	5	80	90	90
35	SL-12	1.06	0.25	D-8	20	50	90	90
36	SL-11	0.1	0.05	D-8	5	30	90	90
37	SL-14	0.456	0.10	D-7	15	50	90	90
38	SL-12	2.13	0.50	D-1	5	50	90	90
39	SL-14	6.0	1.28	D-7	5	30	90	90
40	SL-12	2.0	0.47	D-1	5	30	90	90
41	SL-11	2.0	1.0	D-7	—[c]	50	90	90
42	SL-14	2.33	0.50	D-1	15	30	90	90
43	SL-13	6.17	1.00	D-1	5	70	90	90
44	SL-13	1.54	0.25	D-7	25	70	90	90
45	SL-13	0.62	0.10	D-7	25	30	90	90
46	SL-13	0.62	0.10	D-1	5	30	90	90
47	SL-13	0.62	0.10	D-8	15	30	90	90
48	SL-13	1.54	0.25	D-7	25	70	90	90
49	SL-13	0.62	0.10	D-1	5	30	90	90
50	SL-13	3.05	0.50	D-8	15	70	90	90
51	SL-13	5.95	0.96	D-7	25	50	90	90
56	SL-15	3.0	—[a]	D-7	—[c]	50	90	90

[a] Solid sludge—oil content not defined.

[b] To convert lb/ft^2 loading to barrels/acre, multiply lb/ft^2 by 145. Assumes sludge/oil density = 300 lb/bbl.

[c] Data not obtained.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HEATERS
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HYDROCARBON PROBE
AIR VELOCITY PROBE
AIR INLET
4'
AIR EXIT TO BLOWER 10" DIAMETER
DIFFUSER
REMOVABLE SOIL BOX WITH BURIED HEATER (4" OR 12" DEPTH)
BALANCE
36"
12"
36"
12"
70A3262

Figure 3-2. Laboratory Landtreatment Simulation Apparatus

Air Temperature--

In phase I, the air temperature was controlled with a space heater placed immediately in front of the soil box. This probably allowed a considerable amount of variation in the temperature of the air passing over the sludge. Additionally, this prevented any reasonable effort at controlling the relative humidity. To alleviate this, a three foot long section was added to the inlet end of the apparatus. Several resistance heater elements were installed to heat all incoming air. A feedback controller with a thermistor sensing probe, placed just before the soil box, was employed to maintain a constant 90°F air temperature. Between the heater elements and the temperature probe, a wood fiber diffuser was installed to insure that all of the air crossing the soil box was at the same temperature.

Air Humidity--

During phase I, all but one simulation test was conducted at ambient humidity. However, while the ambient humidity at lab temperature measured about 50%, the measured humidity of the warmed air crossing the soil box was much lower (less than 30%). In the initial testing prior to phase II simulations, a Varsala model HMP-14A humidity sensor was adapted to the data acquisition system. Moisture in the form of steam, was added to the air after it was heated and before mixing in the diffuser by a small "deep fat fryer' installed in the extension box. Power to this unit and therefore the amount of steam, was regulated by manual adjustment of a variac. Water was constantly dropped into the pot (to replace the vaporized water) by a manually controlled perislaltic pump. Output from the humidity probe which was placed just before the soil box, was continually recorded on a strip chart recorder. In general, this system worked well, and constant humidity could be easily achieved.

Soil Boxes--

The removable soil boxes used in phase II had the same surface area as in phase I, one square foot. However, this unit was coupled to the air conditioning chamber and the air monitoring chamber with flexible sheeting.

The box rested on an analytical balance capable of measuring to the nearest 0.01 lb. In this manner, the weight of sludge applied and the weight loss due to volatilization during a run could be determined directly.

VOC/Air Mixing--

In phase II the air mixing/monitoring chamber was three feet long. VOC-laden air coming from the soil chamber was mixed by forcing it around two baffle plates and finally through a diffusion plate containing many 1/8" holes. Initially, verification of adequate mixing was obtained visually through smoke release tests. Additionally, a velocity traverse near the exit showed a relatively constant air velocity throughout the box. However, as in phase I, air velocity very near the edges was somewhat lower than the other areas.

Air Velocity Measurements--

In phase I a Kurtz model 700 Air Velocity Monitor was used. In phase II air velocity was continuously measured with a Met 1 Inc. model 010 wind velocity instrument. Output from this unit is accurate to 1% (0-25 mph range) and was recorded on a strip chart recorder. In all experiments, rapid fluctuations over a narrow velocity range were experienced. However, the average air velocity for all runs was maintained at 3 miles per hour.

VOC Measurement--

In phase I a Bacharach "TLV Sniffer" was used to monitor emitted VOC's. This unit has some pronounced drift problem over very long monitoring periods. However, it does provide a continuous reading of hydrocarbon levels. In the initial simulation runs of phase II, a TLV Sniffer was employed. Additionally, a Byron Instruments model 401 Total Hydrocarbon Analyzer was used. For the long monitoring periods and the very low VOC levels encountered in phase II experiments, reliability of the data from the TLV Sniffer was not adequate. Its use was discontinued shortly after beginning the simulation runs.

The Byron 401, with an analysis cycle time of one minute, resolution of 0.1 ppmv-C and a built-in integrator seemed very adequate for the analysis. An existing microcomputer-based data acquisition system was adapted for the Byron analyzer. This combination was used for all simulation experiments.

Changing VOC Composition--

In each phase I simulation run, an initial surge of VOC emissions was obtained. The level usually dropped rapidly to a much lower value and then slowly declined further. Since identification of the individual hydrocarbons was not accomplished, it was only theorized that very volatile components "flashed off" at the beginning and the heavier compounds were slowly emitted over a much longer period. In order to verify this, VOC-laden air samples were obtained during several simulation runs. These samples were subjected to GC analysis to identify and quantitate the hydrocarbons present.

Long Term VOC Emissions--

Data interpretation in phase I focused on the hydrocarbon emitted during the brief (typically less than 10 minutes) surge obtained soon after spreading and over the 30-minute period following the spreading. This resulted from the apparently overwhelming dominance of VOC's emitted during the relatively short monitoring period. To investigate the somewhat longer term behavior, each of the phase II simulation experiments was monitored for much longer periods generally in the range of 6-8 hours. To further investigate the long term VOC emission levels, several of the boxes were maintained at ambient conditions for several days after the initial monitoring period. These soil boxes were then placed back in the apparatus and monitored for an additional period. Two of these long term test samples were then "tilled" and further monitored for VOC emissions.

Sub-Surface Injection--

Time and budget constraints as well as exhaustion of sludge samples prevented any further work in this area. This type of landtreatment should be further investigated for its potential impact. This is discussed further in the recommendations of Section 6.

3.4.4 Simulation Experiment Procedures

In general, the procedure for the simulation experiments was almost identical to that used in phase I. A step-by-step description is included here for completeness.

1) Prior to a run, the Byron 401 was turned on and its oven brought up to temperature. The air and hydrogen were adjusted to the proper delivery pressures, the flame was lit, and a stable baseline obtained. Proper instrument functioning was verified by analysis of a mixed gas standard containing C_3H_8, CH_4, CO, and CO_2. The instrument was calibrated with the low and high hexane standards to provide a response factor (RF) within the acceptable range of the QC requirements.

2) The soil moisture content was adjusted to the appropriate level by adding water.

3) When steps 1 and 2 were completed, the selected soil box was filled with the soil. The soil heaters were placed at least 1 inch below the soil surface. The box was placed in position (on the balance) and carefully sealed to the air chambers.

4) The equipment for controlling air velocity, air temperature, and relative humidity was started and adjusted. When the air velocity was constant at 3 mph and the air temperature at 90°F, the soil heater was turned on. As soon as the soil temperature stabilized at 90°F, and the humidity was at the desired level, the experiment was continued.

5) The data acquisition system was placed on line (computer and Byron 401) to monitor the background VOC level.

6) The sludge that was to be applied was thoroughly mixed. The proper amount of sludge was then weighed into the application container. The weight of soil box was recorded.

7) When all environmental conditions were correct, the soil box top was removed and the sludge bottle inverted. Nitrogen pressure was used to force the sludge out of the bottle. The sludge was spread evenly over the entire surface of the soil by a small (2-inch wide) "duckbill" spreader device.

8) As soon as all the sludge was spread, the soil box was reinstalled and sealed.

9) The weight of the soil box was recorded, the environmental conditions, such as temperature, air velocity and humidity were also recorded. The time of spreading was indicated on the strip chart paper.

10) Monitoring of the VOC level was continued. After ensuring that the 401 was on the correct scale (maximum upscale but onscale peak height), the meter switch was changed to THC mode so that the integrated THC area was displayed.

11) Periodically during the period of the test run, the following items were monitored and adjusted or recorded as needed:

- Air speed,
- Humidity
- Water level in the pot,
- Soil temperature,
- Air temperature,
- Soil box weight,
- Attenuation setting of the analyzer, and
- Background hydrocarbon level of the air entering the system.

12) At the end of four hours, if the VOC level had fallen to the background level measured in Step 11, the run was terminated. A typical background concentration of VOCs was roughly 0.2 to 0.5 ppmc. If the VOC level was above background, the monitoring was continued for up to 4-5 additional hours. A final weight of the soil box at run termination was also obtained.

3.4.5 Collection and Analysis of Simulation Run Emissions

After emission into the air above the soil, hydrocarbons were swept along by the 3 mph wind maintained in the chamber. Thorough mixing was assured by the baffle and diffuser plates. Analytical data pertaining to this will be given in Section 3.5 covering QC activities.

The hydrocarbon probe consisted of a length of 1/8" Teflon tubing leading from the mixing chamber to the sample inlet of the Byron 401 analyzer. Sample gas was pulled through this line and the internal sample loop by a pump attached to the sample exhaust of the analyzer. The pump, under control of the 401 analyzer, was stopped for 6 seconds prior to sample injection to allow the sample line and loop to bleed to atmospheric pressure.

After injection, the entire sample is swept directly into the flame ionization detector where bond cleavage produces an ion for each carbon atom. Thus, ideally, a molecule of trimethyl benzene, for example, containing 9 carbon atoms will produce a signal which is 9 times greater than that produced by a molecule of methane. A 100 ppm hexane (C_6H_{14}) sample would yield six times the amount of signal (area) as a 100 ppm methane sample.

Another important factor needed for proper interpretation of FID results from the Byron 401 is relative efficiency of the bond cleavage/ion collection or detection system. As the molecular weight increases, this efficiency, or response factor, decreases. It is dependent on the particular detector being used. In particular, the response factor for hexane during calibration averaged about 85% of that obtained for the propane/methane in the mixed gas standard.

The procedure for obtaining gas phase samples for GC analysis was relatively simple. Steel cylinders of about 500 ml volume were cleaned and evacuated to about 75 mm Hg pressure. Attached to the cannister was a shutoff valve and a vacuum flow regulator preset for 25 cc/min. A 1/8" teflon tube delivered VOC-laden air from an area adjacent to the hydrocarbon probe to the regulator.

The actual sampling consisted of opening the valve for 30-60 minutes and then closing it. Analysis of the gas by gas chromatography involved pressurizing the cannister with ultra high purity air and cryogenic trapping of a portion of the sample. This was followed by temperature programmed (from sub-ambient temperatures) chromatography utilizing capillary columns. After separation, the gas was split between a photo-ionization detector and a flame ionization detector. Details concerning the analytical procedure are contained in Reference 2.

3.5 QUALITY CONTROL

To assess and document the precision and accuracy of the data obtained during this project, several quality control procedures were employed. These included systematic calibrations of the THC analyzer with certified standard gases, verification of the mixing chamber operation, comparison of other analytical devices against precision instruments, and recovery testing for the GC-MS system. Each of these is described in the following sections.

3.5.1 THC Analyzer

A Byron 401 analyzer is basically a process GC with two modes of operation. In this project, only the THC analysis mode was used. However, all functions were checked periodically by analysis of a certified gas mixture containing propane, methane, carbon monoxide, and carbon dioxide in zero grade air. The results of this calibration are response factors (RF) for each of the five data channels, i.e., THC, non-methane hydrocarbons (NMHC), CH_4, CO, and CO_2. The flame, air and hydrogen flows as well as carrier air flow were adjusted, if necessary, to provide optimum separation and consistent response factors for the entire group. In addition to these calibrations, blank analyses were performed with zero air to assure that internal sample lines were not contaminated.

Calibration of the Byron 401 in the THC mode was accomplished by determining the THC response factors (RF) for two certified gas standards containing hexane in zero air. These contained 52.6 ppmv and 546 ppmv hexane corresponding to 315.6 ppmv-C and 3216 ppmv-C, respectively. These data, along with blank analysis results, were treated as a multipoint calibration and subjected to linear regression analysis. Proper instrument operation was assumed if the following criteria were met:

- Blank contained less than 0.5 ppmv-C,
- Correlation coefficient was greater than 0.9950,

- Average RF was within 10% of the running mean of all RF's, and
- Coefficient of variation for the RF's was less than 10%.

Initially, calibration was performed on each analytical day. However, with the evident stability of the analyzer, this was broadened to once per week.

The results of all THC analyzer calibrations are given in Table 3-2. These data indicate that the analyzer met all QC requirements during the entire project.

3.5.2 Mixing Chamber

In phase I, calibration of the evaporation/analytical scheme was accomplished by evaporating a weighed amount of hexane and relating this to the integrated analysis data. In phase II, calibration required only assurance that the analyzer would account for all hydrocarbons released into the mixing chamber.

This was accomplished by releasing a known quantity of pure propane into the simulation apparatus and analyzing the propane/air mixture at the exit of the chamber. To obtain the percent recovery, temperature and pressure correction factors for the flow rate were also required.

Recoveries were measured at four different propane flow rates. This simulated a range of hydrocarbon emission rates.

The results of this quality control effort, as summarized in Table 3-3, gave recoveries from 98 to 104%. At the lower flow rates, the propane flow was also measured after completing the test. Recoveries based on the final flow rates are shown in parentheses in Table 3-3.

TABLE 3-2. MULTIPOINT CALIBRATIONS OF THC ANALYZER

Date	Blank[a] Conc (ppmv-C)	Low Standard[b] RF[c]	High Standard[d] RF	Average RF	Correlation[e] Coefficient	Coefficient of Variation (CV)[f] (%)
10/1/82	0	0.8660	0.7926	0.8293	0.99996	6.3
10/4/82	0	.8250	.7767	.8009	.99998	4.3
10/5/82	0	.8536	.7889	.8213	.99997	5.6
10/5/82	0	.8548	.7901	.8225	.99997	5.6
10/7/82	0	.8076	.7767	.7922	.99999	2.8
10/8/82	0	.8387	.7474	.7931	.99993	8.1
10/11/82	0	.8076	.7438	.7758	.99997	5.8
10/18/82	0	.8014	.7682	.7848	.99999	3.0
10/21/82	0	.7989	.7438	.7714	.99998	5.1
10/26/82	0	.7902	.7682	.7792	.99999	2.0
10/27/82	0	.8263	.7865	.8064	.99999	3.5
10/28/82	0	.8151	.8108	.8130	1.00000	0.4
10/29/82	0	.8263	.7926	.8095	.99999	2.9
11/1/82	0	.8673	.7974	.8234	.99997	5.9
11/2/82	0	.8822	.8169	.8496	.99997	5.4
11/3/82	0	.8785	.8206	.8496	.99998	4.8
11/4/82	0	.8499	.7840	.8170	.99997	5.7
11/5/82	0	.8635	.7840	.8238	.99995	6.8
12/28/82	0	.8387	.8108	.8248	.99999	2.4
1/2/83	0	.8064	.7560	.7812	.99998	4.6
1/9/83	0	.8263	.7901	.8082	.99999	3.2
1/9/83	0	.7778	.7377	.7578	.99999	3.7
1/17/83	0	.8511	.7987	.8249	.99998	4.5

[a] Zero grade air analyzed

[b] Certified standard of 52.6 ppm hexane (315.6 ppmv-C) in zero air

[c] RF = Response Factor calculated from RF = (Integrated Area x Attenuation)/(100 x Concentration)

[d] Certified standard of 536 ppm hexane (3216 ppmv-C) in zero air

[e] Calculated from zero and two upscale standards

[f] Calculated from CV = (Standard Deviation/Mean) x 100

TABLE 3-3. RECOVERY STUDY OF PROPANE THROUGH THE MIXING CHAMBER

Nominal Propane Flow Rate (ml/min)	Calculated Propane Emission Rate (lb/hr)	Measured Propane Emission Rate (lb/hr)	Recovery (%)
682	0.172	0.168	97.6
674	0.170	0.175	103
230	0.0581	0.0625	98.4 (107)[a]
69.4	0.0175	0.0182	104 (83.5)[a]

[a] Recovery based on propane flow rate measured after completing test run

3.5.3 Other Analytical Devices

General quality control procedures throughout Radian laboratories call for comparing responses to reference or precision devices being used simultaneously. These included the following:

- The relative humidity probe was to consistently read within 2% of a precision sling psychometer,
- The wind velocity instrument was calibrated to be within its 1% accuracy limits shortly before installation,
- The balance was checked with a class S weight set at least once a week (only up to about 2 pounds), and
- Thermometers were to have an accuracy of better than ±5%.

3.5.4 Recovery Testing for GCMS

Two separate recovery tests were made in the GCMS during the project. The first insured proper instrument functioning through analysis of a standard similar in composition to the sludges. The results of this are given in Table 3-4.

The second test was specific to the sludge samples being analyzed. Each was spiked with 20 ppm each of d_{10}-anthracene and d_8-toluene. The concentration for the measured species was calculated using an RF of 1.5. Results of these tests are given in Table 3-5.

TABLE 3-4. GCMS RECOVERY OF PREPARED STANDARD

Compound	Prepared Concentration (ppm)	Measured Concentration (ppm)	Recovery (%)
Hexachlorobutadiene	20	15	75
Isophorone	50	39	78
Acenaphthene	15	16	106
Fluorene	15	11	73
Hexachlorobenzene	10	5.0	50
Pyrene	25	22	88
Lindane	20	8.3	43

TABLE 3-5. GCMS RECOVERY OF d_{10}-ANTHRACENE OR d_8-TOLUENE IN SLUDGE SAMPLES

Sample ID	Recovery (%)
SL-11	87
SL-12	92
SL-13	84
SL-14	90
SL-15	84
SL-16	87
SL-17	87
SL-18	83
SL-19	98

SECTION 4

EXPERIMENTAL RESULTS

The results of the various tests and analysis performed during the course of this study are summarized and presented in this section of the report. The analyses and interpretation of these results are discussed in the following Section 5.

The results of the soil and sludge characterization studies are presented in Sections 4.1 and 4.2, respectively. The results of the laboratory landtreatment simulation tests are summarized in Section 4.3.

In many cases, the procedures and conditions which were selected and used during phase II of this study resulted from conditions and results observed during phase I of the landtreatment study. For this reason, some of the phase I results are included where pertinent in both this section and the following Section 5. It will be evident from comparing the volatilities of the sludges tested in phase I with those of phase II that the two sludges studied most frequently in phase I were much more volatile than any of the phase II sludges. This was unfortunate because many of the test conditions and equipment designs developed for phase II were based on the phase I results.

4.1 SOIL CHARACTERIZATION RESULTS

Several samples of refinery landfarm soils were obtained from refineries. These were tested to determine the following characteristics:

- pH
- specific gravity

- moisture content
- particle size distribution
- classification (sand, silt, clay)
- oil and grease content
- organic carbon by heating
- organic carbon by titration (oxidizable carbon)

The characterization test results for the refinery soils are shown in Table 4-1. Most of these results are self-explanatory. The large discrepancies between the results for organics content can be partially explained by the differences in the actual parameter being measured. The oil and grease test measures Freon extractable materials. The heating test measures the amount of material volatilized at 500°F. The titration procedure measures material oxidized by $K_2Cr_2O_7$. None of these parameters were used to determine which soils were to be further tested.

The bases for the soil classifications can be clearly seen in Table 4-2. The gradation distributions are shown for each soil. Three soils were used in the land farming simulation studies. They were:

- D-1 (predominantly sand)
- D-8 (predominantly silt)
- D-7 (predominantly clay)

4.2 RESULTS OF SLUDGE TESTING

Those refineries which furnished the sludge and soil samples used in this study also provided information concerning their landtreatment operations. Some of this information, which was supplied in answer to a Radian questionnaire (see Appendix A), is summarized in Tables 4-3 and 4-4. Reported sludge characteristics and landfarming conditions are included in these summaries.

TABLE 4-1. CHARACTERIZATION TEST RESULTS FOR REFINERY SOILS

Soil ID#	pH	Sp. Gr.[c]	Moisture (wt. %)[a]	Soil Classification	Oil & Grease (wt. %)	Organic Carbon (wt %)	
						Heating	Titration
D-1	7.3	2.5	1.9	Silty sand	2.9	8.4	0.07[b]
D-2	5.3	2.2	24	Sandy silt	0.4	15.0	0.34
D-3	7.0	2.3	33	Clayey silt	0.5	11.9	0.26
D-4	4.1	2.0	22	Silt w/sand & clay	2.1	18.9	0.46[b]
D-5	6.8	2.3	13	Silty sand	0.8	10.1	0.28
D-6	6.2	2.5	20	Silty clay w/sand	0.8	9.6	0.09
D-7	7.0	2.5	26	Silty clay	0.1	14.0	0.97[b]
D-8	7.0	2.2	35	Sandy silt	1.1	17.5	0.21

[a] g water per 100g of wet soil.

[b] Average of two determinations.

[c] Specific gravity of solids (particle density), gr/cc.

TABLE 4-2. GRADATION DISTRIBUTION OF LANDFARM SOIL SAMPLES

Sample ID	Gradation Distribution, Wt %						Particle Density, Gr/cc
	Gravel	Coarse Sand	Medium Sand	Fine Sand	Silt	Clay	
D-1[a]	0	0	2	62	30	6	2.43
D-2	0	0	3	26	64	7	2.18
D-3	0	1	2	8	51	38	2.56
D-4	1	0	2	11	74	12	1.83
D-5	1	0	2	53	39	5	2.32
D-6	0	0	2	10	35	53	2.70
D-7[a]	0	0	1	4	23	72	2.53
D-8[a]	0	0	2	18	76	4	2.29

[a] Soils used in landtreatment simulation studies.

TABLE 4-3. SLUDGE DESCRIPTION REPORTED BY PARTICIPATING REFINERIES

Sludge ID	Source Refinery		Sludge Type/Source	Sludge Production Rate	Sludge Sample Source	Sludge Pretreatment Before Landfarming
	Type	Size Range[a]				
SL-11	Integrated	A	Tank Bottoms Separators Cooling Water Towers Holding Pond Emulsions	60,000 lb/yr 800,000 lb/yr 400,000 lb/yr 1,800,000 lb/yr	Emulsion from Wastewater Holding Pond	Weathering, Oil Separation in API Separator
SL-12	Integrated	C	3-5% oil, 8% dirt/sand 84% water, 3% activated carbon	120 tons/day	Dissolved Air Flotation Unit	Dewatering
SL-13	Integrated	B	Tank Bottoms DAF Froth API Bottoms Biological Oxidation Sludge	1500 yd^3/yr 3600 yd^3/yr 5000 yd^3/yr 2 gal/min	Mixture of API Separator Bottoms, DAF Froth, Biological Oxidation Sludge-15% Solids, 13% Oil, 72% Water	Decanting of Oil and Water in Sludge Pond
SL-14	Lube	B	Non-Leaded Tank Bottoms API Separator Sludge Slop Oil Emulsion Solids Coker Blowdown Sludge Spent Clay from Kerosene Treating Miscellaneous Oily Solids	200 tons/yr (≤65% oil) 38 tons/yr (3-19% oil) 175 tons/yr (5-75% oil) 15 tons/yr (20-30% oil) 200 tons/yr (~3.5% oil) 25 tons/yr	API Separator Sludge	None
SL-15	Integrated	C	Tank Bottoms (30% oil, 25% H_2O) Separators (50% oil, 5% H_2O) Jet Filter Clay (35% oil, 6% H_2O)	500 bbl/yr 200 bbl/yr 3600 bbl/yr	Jet Filter Clay	None
SL-16	Integrated	B	Emulsion Plant Filter Cake (40% oil, 40% H_2O)	2.5 tons/week @6 days/week	Emulsion Plant Vacuum Filtercake	None
SL-17	Petrochemical	B	Tank Bottoms Separators Biological Oxidation	15,000 bbl/yr 50,000 bbl/yr 55,000 bbl/yr	Separator Sludge Biological Oxidation Sludge	Separator Sludge-Emulsion Breaking and Gravity Thickening. Biological Sludge - Aerobic Digestion
SL-18	Cracking	B	Misc. Tank Bottoms (14-30% oil) Biological Oxidation Sludge (1.5% oil) DAF Float (1.5% oil) API/CPI Separator (10-20% oil)	480 tons/yr 2450 tons/yr 2450 tons/yr 200 tons/yr	Biological Oxidation Sludge	Thickening

[a] Size Ranges:
A = ≤ 100,000 BPD
B = 100,000 - 200,000 BPD
C = > 200,000 BPD

TABLE 4-4. SUMMARY OF SLUDGE LANDTREATMENT CONDITIONS FROM PARTICIPATING REFINERIES

Sludge ID	Landfarm Soil Type (Reported)	Sludge Application Method	Sludge Application			Seasons Applied
			Rate	Frequency	Sludge Temperature	
SL-11	Sandy Clay	Spread via vacuum truck	800,000 lb/acre	once/three years	Ambient	--
SL-12	Loam	Dumped directly on ground from transportation box, weathered two days, and then spread	300-1000 tons/month per 3 acre plots (until plots are full)	--	Ambient	All
SL-13	--	Sprayed	182,000 gal/acre-year	6 applications per acre per year	Ambient	May-October
SL-14	--	Sprayed from vacuum truck	155 tons/acre	once/2-3 years (for this sludge)	90-100°F	March-December
SL-15	Sandy	Wastes are spread and tilled into soil by tractor	300 bbl/ acre-year	once/month	Ambient	All
SL-16	Clay	Piled, spread, and tilled into soil	50 bbl oil/acre-quarter (200 bbl oil/acre-year)	4/year	--	April-November
SL-17	--	Subsurface injection @ depth of approximately 6"	2500 bbl/acre-year	7/year	Ambient	All
SL-18	Sandy Clay	Poured from vacuum trucks	800 bbl/acre	5/year	Ambient	All

TABLE 4-5. CHARACTERIZATION TESTS RESULTS FOR REFINERY SLUDGES

Sludge ID#	Centrifugation Test (vol %)			Oil and Grease (wt %)		GCMS[a] (µg/gm)	Volatility Test[b] (ppm/ml)
	H_2O	Solids	Oil	I.R.	Grav		
Study Phase: Phase II (Current)							
SL-11	25	12.5	62.5	8.4	21.5	6,103	821
SL-12	40	25	35	0.38	1.1	685	71
SL-13	65	15	20	0.16	2.2	2,914	124
SL-14	70	5	25	0.14	2.2	787	103
SL-15	--	100	--	6.7	14.8	2,796	268[c]
SL-16	--	100	--	0.71	1.9	3,162	136[c]
SL-17	80	7.5	12.5	0.35	1.2	1,314	71
SL-18	5	85	10	0.11	0.4	80	5.1
SL-19	--	100	--	10.3	5.3	10,536	191[c]
Study Phase: Phase I							
T	50	40	10	6.0	11.2	36	(217)
S1	0	6	94	60.9	78.2	347,700	(14,260)
S3	79	15	6	16.0	19.1	277,000	(263,000)

[a] Values are the sum of the concentrations of all identified compounds.

[b] Average hydrocarbon concentration in the stripping gas over a 4-hour test period, normalized to a sludge sample size of 1000 µl (1 ml). Values in parentheses are adjusted values obtained during a 1-hour test period in Phase I.

[c] Values are ppm/gm.

The characterization test results for refinery sludges are summarized in Table 4-5. Included in this table are some of the characteristics of the three sludges tested and used during the phase I study.

The centrifugation tests were performed to provide an estimate of the relative volumes of oil, water, and solids in each of the liquid sludge samples. Centrifugation of the liquid sludge samples generally produced three distinct layers of material. The top, middle, and bottom layers were assumed to be oil, water, and solids, respectively. Obviously there are some limitations associated with this type of analysis. In come cases, emulsions (or emulsified material) were present, and the exact separation point between layers was difficult to discern. Centrifugation does not isolate water-soluble organic material, or oil which is included in the "solids" portion (oil occluded to solids and organic material which is denser than water). The apparent oil content of the phase II sludges varied considerably from 10% (SL-18) to 63% (SL-11). The water and solids content appeared to vary even more. The solids content ranged from 5% to 85%, while the water content varied between 5% and 80%.

Oil and grease tests were performed by extraction with Freon followed by I.R. analyses or gravimetric determinations. The results obtained by these two methods did not agree for any of the tested sludges. The estimated oil and grease levels were considerably below the oil levels estimated from centrifugation results.

The phase II sludges were subjected to GC/MS analyses, and selected hydrocarbons in the C_6- C_{20} range were determined. The total concentration of all identified compounds is included in Table 4-5. The individual concentrations of these selected compounds are presented in Table 4-6. Since only certain selected compounds are reported, the sums should not be assumed to be an accurate measure of the volatility of the sludges. For comparison, some of the results of the GC/MS analyses of the phase I sludges are included in Table 4-6.

TABLE 4-6. SELECTED HYDROCARBON CONCENTRATION IN SLUDGES
(Concentrations are in μg/gm as measured by GCMS)[a]

Compound	Sludges (Phase II)									Sludges (Phase I)		
	SL-11	SL-12	SL-13	SL-14	SL-15	SL-16	SL-17	SL-18	SL-19	T	S1	S3
Benzene	540	32	18	5	14	20	160	38	250	ND	1,800	1,400
Toluene	1,700	58	98	.14	ND	ND	150	36	2,200	0.02	9,300	5,600
M/P-Xylene	700	58	110	30	24	350	40	ND	1,400	1.2	23,000	15,000
O-Xylene	330	28	50	16	11	170	17	ND	510	0.55	42,000	32,000
C_3-Benzene	1,100	150	400	160	1,300	1,000	76	ND	2,800	7.9	222,000	160,000
C_3-Benzene	890	120	400	140	620	900	60	ND	2,100	NR	NR	NR
Naphthalene	230	34	350	64	ND	50	500	ND	400	NR	NR	NR
Anthr./Phen.	150	20	1,100	92	20	210	120	ND	150	NR	NR	NR
C_9-H.C. (alkane)	130	30	14	36	160	8	13	ND	180	NR	NR	NR
C_{12}-H.C. (alkane)	140	57	210	120	410	200	44	ND	230	NR	NR	NR
C_{17}-H.C. (alkane)	84	72	84	68	120	84	60	6	130	NR	NR	NR
C_{17}-H.C. (alkane) (pristane)	66	72	24	68	99	84	34	6	78	NR	NR	NR
C_{19}-H.C.	31	26	40	28	18	54	14	ND	70	NR	NR	NR
C_{20}-H.C.	2	NM	16	14	ND	32	26	ND	38	NR	NR	NR

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[a] Light aromatics quantitated based on d_8-toluene. Naphthalene, anthr./phen., and alkanes based on d_{10}-anthracene.

Stripping or volatility tests were performed on the fresh sludge samples prior to any landtreatment simulation tests. Cumulative average hydrocarbon concentrations in the stripping gas (nitrogen) were continually determined over the duration of each test. Several sludge sample sizes were used in the tests. For comparative purposes, the four-hour average concentrations were normalized to sample sizes of 1000 ul (1 ml). The results of the detailed volatility tests on the fresh sludge samples are shown in Table 4-7. The normalized average concentrations for the four hour test period are also included in Table 4-7. However, the hourly results shown in Table 4-7 are not normalized.

The results of the volatility tests on the three sludges from the phase I study are also included in Table 4-7. It can be seen that the normalized volatilities of the two liquid sludges, S1 and S3, are higher by several orders of magnitude than those of any phase II sludge. It would appear that the phase I liquid sludges, particularly sludge S1, were not particularly representative of the types of sludges normally landtreated at refineries.

The tests were performed over a period of approximately seven months. It was found that some of the sludge samples apparently had lost volatile material, probably due to unrefrigerated storage and periodic opening of the sample containers. Sludge samples were taken at the end of the test period, and were subject to additional stripping tests. The initial and final volatilities were then used to prepare weighted volatilities for each simulation test. These weighted volatilities, listed in Table 4-8, were later used in developin the emission model.

4.3 RESULTS OF LABORATORY LANDTREATMENT SIMULATION TESTING

A number of individual landtreatment simulation tests were performed during this study. A total of 42 of these tests had durations of 4 hours or more. Several other tests were attempted, but the runs were aborted because of equipment malfunctions or otherwise unsatisfactory performances. Those tests lasting for four or more hours were considered to be acceptable, and the results were included in the data analysis.

TABLE 4-7. VOLATILITY TEST RESULTS (INITIAL TESTING)

Sample ID #	Sample (µl)	Average Hydrocarbon Concentration (Hexane Equivalent) During the Period, ppm[d]						Normalized 4 hr ave.[b] (ppm/ml)
		1st hour	2 hours	3 hours	4 hours	5 hours	6 hours	
Study Phase:	Phase II (Current):							
SL-11	50	125	69	49	37	NA	NA	720
	1000	1957	1311	1001	821	699	611	821
SL-12	1000	141	104	85	72	64	57	72
	1000	169	112	85	69	58	50	69
SL-13	250	228	175	145	126	112	102	504
	1000	226	174	145	124	109	97	124
	250	143	106	86	73	64	57	292
SL-14	100	145	86	62	48	40	34	480
	1000	253	162	120	96	80	69	96
	100	104	62	45	35	29	25	350
	1000	272	180	136	110	92	79	110
SL-15	1000	1135	684	504	401	333	288	401[a]
	1000	341	214	163	134	114	99	134[a]
SL-16	1000	197	172	152	136	122	111	136[a]
SL-17	100	70	42	30	24	20	17	240
	1000	196	120	89	71	60	52	71
	100	26	15	11	9.5	8.1	7.1	95
SL-18	100	8.3	5.4	4.3	3.7	3.3	3.0	37
	1000	6.6	5.8	5.4	5.1	4.8	4.6	5.1
SL-19	1000	514	321	239	191	160	138	191[a]
Study Phase:	Phase I:							
S1	1	263[c]	-	-	-	-	-	263,000
S2	5	72[c]	-	-	-	-	-	14,300
T	20	4.4[c]	-	-	-	-	-	217

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[a] Values are in ppm/mg.
[b] Concentrations are normalized to sample sizes of 1000 µl (1 ml).
[c] Adjusted for nitrogen purge rate of 200 ml/min.
[d] Concentrations are the cumulative average concentrations over the entire periods from the start of the study.

TABLE 4-8. WEIGHTED SLUDGE VOLATILITIES

Experimental Run No.	Sludge ID No.	Weighted Sludge Volatility, Average 4 Hour Concn., ppm/ml
2	SL-11	821
5	SL-11	821
6	SL-11	821
7	SL-12	72
8	SL-14	96
9	SL-14	96
10	SL-11	760
11	SL-11	760
12	SL-11	760
13	SL-14	96
15	SL-11	570
16	SL-11	570
17	SL-12	22
18	SL-14	30
19	SL-12	22
20	SL-12	22
21	SL-11	550
22	SL-11	540
23	SL-11	540
24	SL-14	22
25	SL-11	530
26	SL-11	530
27	SL-11	530
28	SL-14	16
29	SL-14	16
32	SL-11	510
33	SL-11	510
34	SL-14	13
35	SL-12	14
36	SL-11	510
37	SL-14	12
38	SL-12	13
39	SL-14	12
40	SL-12	7
41	SL-11	480
42	SL-14	5
43	SL-13	85
44	SL-13	85
45	SL-13	85
46	SL-13	85
47	SL-13	85
48	SL-13	85
49	SL-13	85
50	SL-13	85
51	SL-13	85

The experimental conditions for the successful tests were listed previously in Table 3-1. The air and soil temperatures were maintained at 90°F during all testing. Air speed was held at 3 miles per hour. The parameters which were varied during the testing included sludge type, sludge loading, soil type, soil moisture content and the relative humidity of the air.

The results of the tests are summarized in Table 4-9. The cumulative VOC emissions measured at times of 0.5 to 8 hours from sludge application are presented. Most runs were continued for 7 hours, and about half lasted 8 hours or more. The VOC emissions are expressed as pounds emitted per square foot of landtreatment surface, percent of applied oil and as percent of applied sludge. The percentage of oil in the sludges is based on the results of the sludge centrifugation tests.

(For comparative purposes, the results of phase I landtreatment simulations are briefly summarized in Table 4-10. The phase I simulation experiments were only continued for a short period, generally less than one hour. Thus, only the emissions at 30 minutes are reported. The experimental conditions for each phase I test run are given in Appendix C.)

During the phase II testing, samples of the air coming from the soil chamber were collected in evacuated stainless steel canisters. The contents of these canisters were then analyzed by cryogenic GC techniques. The results of these analyses are summarized in Table 4-11. Total non-methane hydrocarbon (TNMHC) levels ranged from 0.82 ppmv-C (Run 30, Canister 11) to 30.42 ppmv-C (Run 41, Canister 11) or from 0.14 to 5.07 ppmv as hexane. The concentration in most of the air samples was between 1 and 3 ppmv as hexane.

The complete results of the individual sample analyses are contained in Appendix D. Species are reported in order of their elution. Only those species which were present at concentrations equal to or greater than 10 ppbv-C were reported.

NOT REPRODUCIBLE

TABLE 4-9. EXPERIMENTAL RESULTS OF LANDTREATMENT SIMULATIONS (PHASE II STUDY)

			Cumulative VOC Emissions[c]														
			Elapsed Time = 30 minutes			Elapsed Time = 120 minutes			Elapsed Time = 240 minutes			Elapsed Time = 420 minutes			Elapsed Time = 480 minutes		
Run ID No.	Sludge ID No.	Sludge Loading,[b] Lb Oil Per Ft²	VOC, Lb per Ft²	VOC, % of Applied Oil	VOC, % of Applied Sludge	VOC, Lb per Ft²	VOC, % of Applied Oil	VOC, % of Applied Sludge	VOC, Lb Per Ft²	VOC, % of Applied Oil	VOC, % of Applied Sludge	VOC, Lb Per Ft²	VOC, % of Applied Oil	VOC, % of Applied Sludge	VOC, Lb Per Ft²	VOC, % of Applied Oil	VOC, % of Applied Sludge
2	SL-11	1.0	0.0401	4.0	2.0	—	—	—	—	—	—	—	—	—	—	—	—
5	SL-11	1.0	0.0154	1.5	0.77	0.0355	3.6	1.78	0.0431	4.3	2.16	—	—	—	—	—	—
6	SL-11	0.3	0.00424	1.4	0.71	0.00922	3.1	1.54	0.0124	4.1	2.07	0.0157	5.2	2.62	—	—	—
7	SL-12	0.40	0.00356	0.7	0.17	0.00503	1.0	0.24	0.0701	1.4	0.33	0.00905	1.8	0.43	—	—	—
8	SL-14	0.45	0.00496	1.1	0.24	0.0109	2.4	0.52	0.0143	3.2	0.68	—	—	—	—	—	—
9	SL-14	0.32	0.00153	0.5	0.10	0.00363	1.1	0.24	0.00579	1.8	0.39	—	—	—	—	—	—
10	SL-11	1.05	0.00420	0.4	0.20	0.0160	1.5	0.76	0.0218	2.1	1.04	—	—	—	—	—	—
11	SL-11	1.0	0.00256	0.3	0.13	—	—	—	—	—	—	—	—	—	—	—	—
12	SL-11	0.3	0.00515	1.7	0.86	0.0127	4.2	2.12	0.0179	6.0	2.98	0.0251	8.4	4.18	—	—	—
13	SL-14	0.49	0.00284	0.6	0.12	0.0153	3.1	0.67	0.0228	4.6	0.99	0.271	5.5	1.18	—	—	—
15	SL-11	0.5	0.00707	1.4	0.71	0.0138	2.8	1.38	0.0216	4.3	2.16	0.0301	6.0	3.01	—	—	—
16	SL-11	0.5	0.00471	0.9	0.47	0.0123	2.5	1.23	0.0184	3.7	1.84	0.0251	5.0	2.51	—	—	—
17	SL-12	0.5	0.00008	0.02	0.00	0.00008	0.02	0.00	0.00030	0.06	0.01	0.00075	0.15	0.04	—	—	—
18	SL-14	0.10	0.00042	0.4	0.09	0.00157	1.6	0.34	0.00265	2.7	0.57	0.00798	8.0	1.71	0.00907	9.1	1.94
19	SL-12	0.25	0.00023	0.1	0.02	0.00055	0.2	0.05	0.00071	0.3	0.07	—	—	—	—	—	—
20	SL-12	1.50	0.00012	0.01	0.00	—	—	—	—	—	—	—	—	—	—	—	—
21	SL-11	0.5	0.00247	0.5	0.25	0.0102	2.0	1.02	0.0157	3.1	1.57	0.209	4.2	2.09	0.0221	4.4	2.21
22	SL-11	2.0	0.00102	0.1	0.03	0.00554	0.3	0.14	0.0129	0.6	0.32	—	—	—	—	—	—
24	SL-14	0.32	0.00007	0.02	0.00	0.0-007	0.02	0.00	0.00007	0.02	0.00	0.00007	0.02	0.00	0.00007	0.02	0.00
25	SL-11	0.75	0.00356	0.5	0.24	0.00826	1.1	0.55	0.0134	1.8	0.89	0.0176	2.4	1.17	—	—	—
26	SL-11	0.05	0.00102	2.0	1.02	0.00205	4.1	2.05	0.00262	5.2	2.62	0.00292	5.8	2.92	—	—	—
27	SL-11	0.05	0.00015	0.3	0.15	0.00028	0.6	0.28	0.00028	0.6	0.28	0.00028	0.6	0.28	0.00028	0.6	0.28
28	SL-14	1.00	0.00001	0.0	0.00	0.00001	0.0	0.00	0.00001	0.0	0.00	0.00001	0.0	0.00	0.00001	0.1	0.00
29	SL-14	0.46	0.00004	0.01	0.00	0.00015	0.03	0.00	0.00032	0.07	0.02	—	—	—	—	—	—
32	SL-11	0.59	0.00531	0.9	0.45	0.0101	1.7	0.86	0.0133	2.3	1.14	0.0167	2.8	1.43	0.0177	3.0	1.51
33	SL-11	1.17	0.0062	0.5	0.26	0.0158	1.4	0.68	0.0210	1.8	0.90	0.0285	2.4	1.22	0.0304	2.6	1.30
34	SL-14	1.28	0.00011	0.01	0.00	0.00012	0.01	0.00	0.00012	0.01	0.00	0.00012	0.01	0.00	0.00012	0.01	0.00
35	SL-12	0.25	0.00028	0.1	0.03	0.00063	0.3	0.06	0.00133	0.5	0.13	0.00211	0.8	0.20	0.00236	0.9	0.22
36	SL-11	0.05	0.00395	7.9	3.95	0.0136	27.2	13.6	0.0220	44.0	22.0	0.0384	76.7	38.4	0.0393	78.7	39.3
37	SL-15	0.10	0.00061	0.6	0.13	0.00271	2.7	0.58	0.00593	5.9	1.27	0.00921	9.2	1.97	0.00986	9.9	2.11
38	SL-12	0.50	0.00024	0.05	0.01	0.00084	0.17	0.04	0.00185	0.37	0.09	0.00442	0.9	0.21	—	—	—
39	SL-14	1.28	0.00067	0.05	0.01	0.00281	0.2	0.05	0.00592	0.5	0.10	0.00898	0.7	0.15	—	—	—
40	SL-12	0.47	0.00014	0.02	0.00	0.00047	0.1	0.02	0.00108	0.2	0.05	0.00278	0.6	0.14	0.00347	0.7	0.17
41	SL-11	1.0	0.00461	0.46	0.23	0.0115	1.2	0.58	0.0179	1.8	0.90	0.0254	2.5	1.27	0.0278	2.8	1.39
42	SL-14	0.50	0.00024	0.05	0.01	0.00028	0.05	0.01	0.00030	0.05	0.01				—	—	—
43	SL-13	1.00	0.0015	0.2	0.02	0.00393	0.4	0.06	0.00976	1.0	0.16	0.0154	1.5	0.25	—	—	—
44	SL-13	0.25	0.00079	0.3	0.05	0.00261	1.0	0.17	0.00563	2.3	0.37	0.0107	4.3	0.69	0.0123	4.9	0.80
45	SL-13	0.10	0.00326	3.3	0.53	0.0115	11.5	1.85	0.0256	25.6	4.13	0.0445	44.5	7.18	0.0499	49.9	8.05
46	SL-13	0.10	0.00027	0.3	0.04	0.00108	1.1	0.17	0.00318	3.2	0.51	0.00684	6.8	1.10	0.00773	7.7	1.25
47	SL-13	0.10	0.00030	0.3	0.05	0.00104	1.0	0.17	0.00251	2.5	0.40	0.00583	5.8	0.94	0.00687	6.9	1.11
48	SL-13	0.25	0.00050	0.2	0.03	0.00158	0.6	0.10	0.00417	1.7	0.27	0.0101	4.0	0.66	0.0124	5.0	0.81
49	SL-13	0.10	0.00045	0.5	0.07	0.00168	1.7	0.27	0.00408	4.1	0.65	0.00896	8.4	1.45	0.00969	9.7	1.56
50	SL-13	0.50	0.00016	0.03	0.01	0.00033	0.07	0.01	0.00125	0.3	0.04	0.00427	0.9	0.14	0.00364	1.1	0.18
51	SL-13	0.96	0.00033	0.03	0.01	0.00081	0.08	0.01	0.00147	0.15	0.02	0.00354	0.37	0.06	0.00452	0.47	0.08
56	SL-13	—[a]	0.00254	—	0.08	0.0115	—	0.18	0.0201	—	0.67	0.024	—	0.80	—	—	—

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[a] Solid sludge—oil content not defined.
[b] Applied oil estimated from volume percent oil determined by centrifugation.
[c] Loading and emissions can be converted from lb/ft² to kg/m² by multiplying lb/ft² by 4.89.
[d] Loading can be converted from lb/ft² to bbl/acre by multiplying lb/ft² by 165.

TABLE 4-10. RESULTS OF LANDTREATMENT SIMULATION DURING PHASE I STUDY

Run ID No.	Sludge ID No.	Sludge Loading, lb Oil per ft^2	VOC Emissions @ 30 Minutes Elapsed Time		
			VOC, lb per ft^{2a}	VOC, % of Applied Oil^a	VOC, % of Applied Sludge
6	S1	2.35	0.0174	0.79	0.70
7	S1	2.35	0.0139	0.63	0.56
9	S1	2.35	0.0119	0.54	0.48
10	S1	0.94	0.0319	3.6	3.2
11	S1	0.94	0.0304	3.5	3.0
12	S1	2.35	0.0513	2.3	2.1
13	S1	2.35	0.0588	2.7	2.4
14	S1	2.35	0.0260	1.2	1.0
15	T	0.25	0.0002	0.90	0.009
16	S1	2.35	0.0159	0.72	0.63
17	S1	3.76	0.0181	0.52	0.45
19	S1	0.47	0.0137	3.1	2.7
19	S1	2.35	0.0165	0.75	0.66
20	S3	0.06	0.0022	1.1	0.22
21	S3	0.15	0.0011	0.22	0.045
22	S3	0.24	0.0035	0.44	0.088
23	S3	0.06	0.0011	0.56	0.11
24	S3	0.24	0.0026	0.33	0.066
27	S3	0.15	0.0018	0.36	0.071

[a] Loading and emissions can be converted from lb/ft^2 to kg/m^2 by multiplying lb/ft^2 by 4.89.
[b] Loading in lb/ft^2 can be converted to bbl/acre by multiplying lb/ft^2 by 145.
[c] Volume fraction of oil in sludge was estimated from centrifugation results.

TABLE 4-11. SUMMARY OF AIR SAMPLE ANALYSES

	TNMHC		
Sample	ppmv-C_6	ppmv-C	Major Species (ppbv-C)
Run 29/Canister 2	0.43	2.58	C_2 (527) C_3 (331)
Run 29/Canister 6	0.21	1.26	Toluene (199) 2,2,5-Trimethylhexane (170.5)
Run 30/Canister 15	0.14	0.83	Toluene (127) 2,5-Dimethylhexane (89)
Run 30/Canister 11	0.14	0.82	Benzene (299) Toluene (117)
Run 31/Canister 7	0.18	1.03	2.4-Dimethylpentane (376) 2,5-Dimethylhexane (111)
Run 39/Canister 7	0.37	2.22	Methylene Chloride (1318) C_2 (94)
Run 41/Canister 11	5.07	30.42	m & p Xylene (2382) n-Nonane (1731)
Run 42/Canister 2	0.42	2.54	Isobutene (192) C_2 (166)
Run 43/Canister 10	0.23	1.35	C_2 (163) n-Undecane (78)
Run 51/Canister 16	1.48	8.90	n-Undecane (894) n-Decane (456)
Run 51/Canister 68	0.31	1.83	n-Undecane (109) Toluene (64)

SECTION 5

DISCUSSION OF RESULTS

The experimental results have been analyzed to provide some insight into the magnitude and composition of VOC emissions from land treatment operations. The effects of the various tested parameters on emissions are discussed in Section 5.1. This section also contains a model for the relationship between the important operational variables and the magnitude of emissions at a given time period.

Section 5.2 contains a discussion of the effect of elapsed time (from the time of application) on the emission rates. The compositions of the sludges and the atmospheric VOC emissions are described and compared in Section 5.3. Some theoretical models have been proposed in the literature to describe the emission rates of VOC from landfarm operations. The verification efforts using data from this current testing are described in Section 5.4.

5.1 EFFECT OF EXPERIMENTAL PARAMETERS ON LAND TREATMENT EMISSIONS

The total VOC emissions at four hours after sludge application was selected for correlation with those experimental parameters studied in the program. The four-hour emissions were chosen (rather than eight-hour emission levels) because there were more data available at this time than at the longer period. However, the relationship between four-hour and eight-hour data was studied. The ratio of mass emission at seven hours to that at four hours is 1.82 with a standard deviation of 0.57 (31%). Similarly, the eight-hour four-hour emission ratio was found to be 2.31 with a standard deviation of 0.76 (33%). The relationship of the four-hour emissions to the seven- and eight-hour values are shown graphically in Figures 5-1 and 5-2. Both the statistical analysis and the graphical presentation indicate a relatively

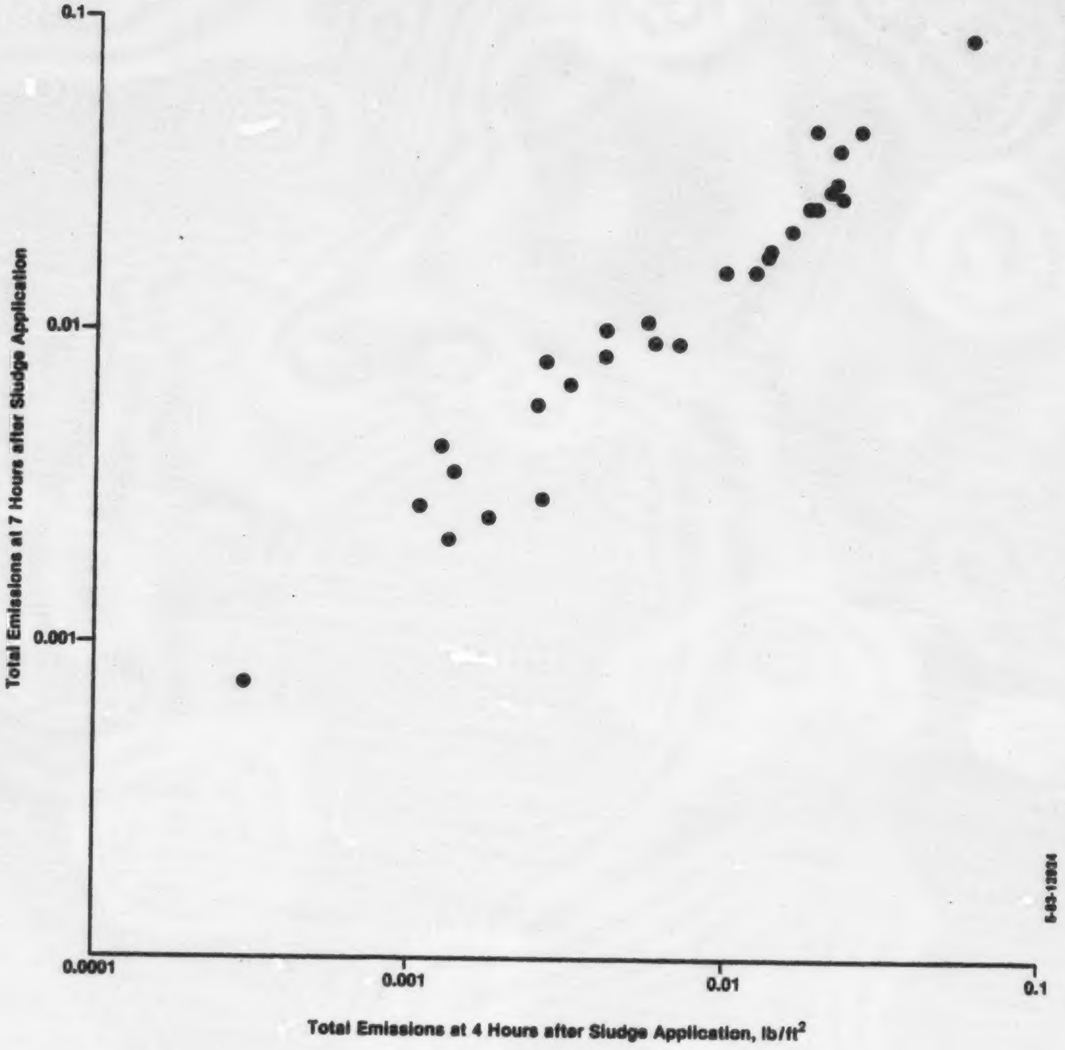


Figure 5-1. Emissions at Four Hours and Seven Hours After Sludge Application

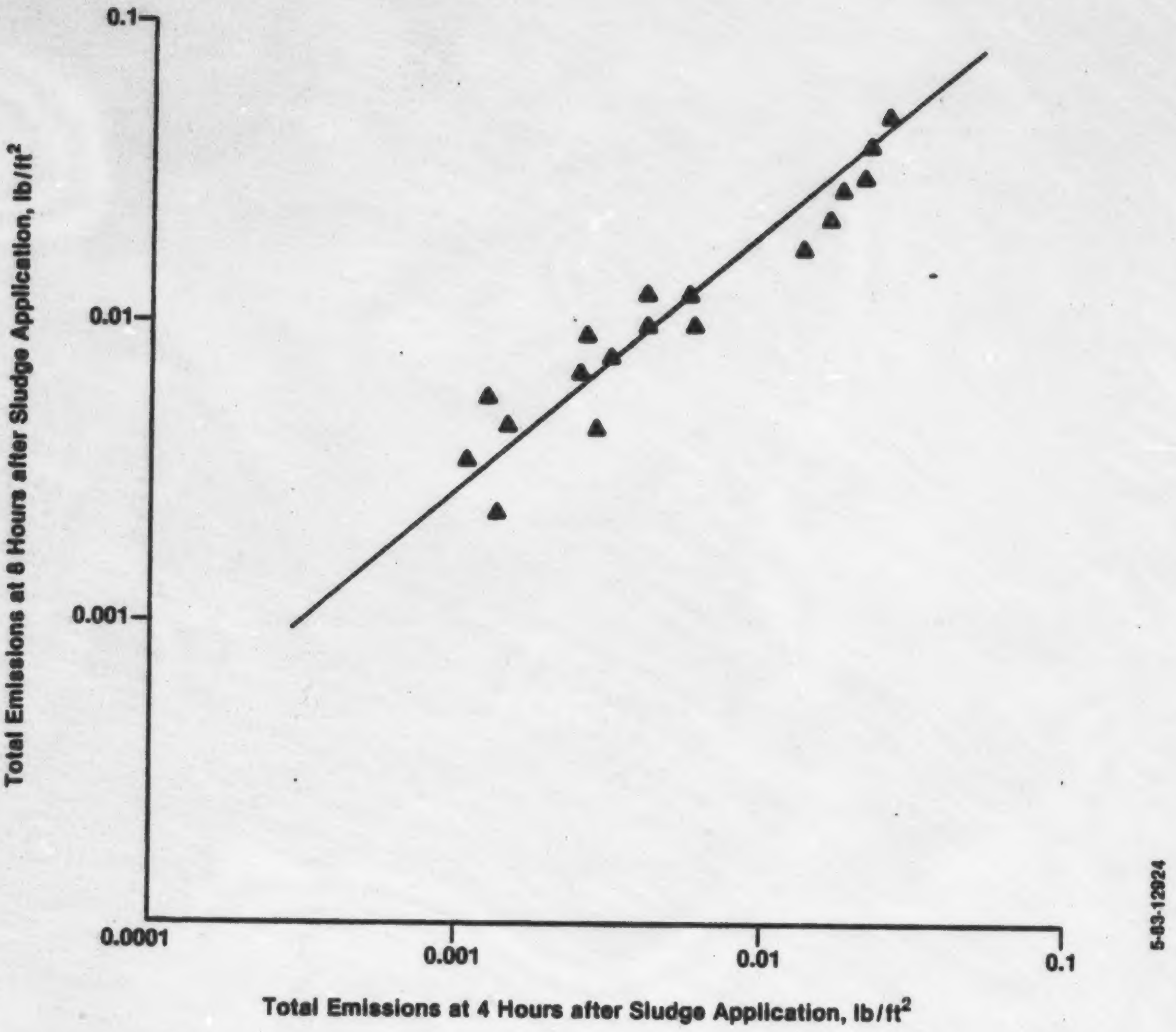


Figure 5-2. Emissions at Four Hours and Eight Hours After Sludge Application

strong relationship between four-hour and seven/eight-hour emissions. There is little reason to believe that relationships developed from the four-hour emission results would not also apply to the seven- and eight-hour emission results.

Multiple regression techniques were used to evaluate a number of mathematical models relating the emissions level to various parameters and combinations of parameters. Table 5-1 contains a list of these parameters and their combinations considered in the several proposed first and second degree models. In addition, models incorporating the logarithmic transform of the four-hour emissions and/or the sludge volatility were tested. Models of various forms, including a full 15-term quadratic were examined.

Preliminary fitting of the full quadratic as well as reduced models identified the following parameters as the only ones which appeared to have a significant affect on the emission levels:

- sludge volatility (V), ppm/ml
- sludge loading (L), lb oil/ft^2 soil
- air humidity (H), %

The emissions level, E (lb/ft^2), was plotted as a function of sludge volatility, V (ppm/ml), and sludge loading, L (lb oil,ft^2), simultaneously. The model predictions were compared with measurements, and Cook's D influence statistic and residuals were examined. Three of the data points were identified as "unusual" compared to all others. The "unusual" characteristics cannot be explained by or related to humidity, soil moisture content, or soil type. The three points (Test Runs 22, 45, 36) were removed from consideration. Comments regarding these test runs are summarized in Table 5-2.

Run No. 22 had the highest oil loading of any of the test runs. The oil loading of 2.0 lb/ft^2 (9.8 kg/m^2) was almost twice that of the next highest oil loading of 1.25 lb/ft^2 (6.1 kg/m^2). Yet the emission rate appeared to be

TABLE 5-1. PARAMETERS AND COMBINATIONS OF PARAMETERS CONSIDERED IN STATISTICAL ANALYSIS OF RESULTS

- Sludge Volatility (4 hour stripping results), ppm/ml
- Air Humidity, %
- Soil Type
- Soil Moisture Content, wt %
- Sludge Loading on Soil, lb/ft^2
- $(\text{Sludge Volatility})^2$
- $(\text{Air Humidity})^2$
- $(\text{Soil Moisture Content})^2$
- $(\text{Sludge Loading})^2$
- (Sludge Volatility) x (Soil Moisture Content)
- (Sludge Volatility) x (Air Humidity)
- (Sludge Volatility) x (Sludge Loading)
- (Soil Moisture Content) x (Air Humidity)
- (Soil Moisture Content) x (Sludge Loading)
- (Air Humidity) x (Sludge Loading)

TABLE 5-2. TEST RUNS OMITTED FROM FINAL DATA EVALUATION AND MODELING

Run Number	Comments
36	The ratio of emissions (E) to loading (L) was very high compared to those of the retained test runs. The ratio of E/L was 0.44 for run 36. The highest ratio in any retained run is 0.06.
45	The ratio E/L was also very high at 0.26.
22	This run has the highest loading (2.0 lb oil/ft^2) of any test. The next highest loading value in any test run was 1.28 lb oil/ft^2 (Runs #34 and 39). The test values were clearly outside the pattern of results obtained with this same sludge at similar conditions at lower loadings.

much lower than other tests run at lower loadings and conditions that were not greatly different than those of Run No. 22.

Run No. 36 produced an extremely high percentage of oil emitted after four hours (44.0%) and longer (78.7% at eight hours). These emission percentages were very much higher than any observed in other runs (except Run No. 45). The oil loading from Run No. 36 was apparently at the lowest level of 0.05 lb/ft^2 (0.24 kg/m^2). At this level, some uncertainties exist regarding both the uniformity of spreading, the homogeneity of the applied sludge sample, and the weight of applied sludge. Because the percentage of emissions was an order of magnitude higher than other tests, it appeared that either some experimental problems or uncertainties had been encountered in this run, or that the loading was so low that the mechanism of vaporization was substantially different from other runs.

Run No. 45 also showed very high emissions (49.9% after eight hours). This run was also made at a relatively low oil loading of 0.10 lb/ft^2 (0.49 kg/m^2). The data from Run No. 45 was not included in the model development for the same reasons given for Run No. 36.

Some experimentation with various model formulations produced several alternative models in V, L, and H. These models were generally simple. The correlations were quite good, with correlation coefficients (r) ranging from 0.92 to 0.94.

The model containing the parameters (H, L, and V) which appears to be simple and most descriptive is shown below.

$$E = aVL\,[H(100-H)]^d + g\,, \qquad \text{(Eqn. 5-1)}$$

where

E = total emissions at four hours, lb/ft^2,

V = sludge volatility (measured during four-hour stripping test, ppm/ml),

L = sludge oil loading on soil, lb oil/ft^2 (oil content of sludge estimated by centrifugation),

H = relative humidity, %,

$a = 6.94 \times 10^{-14}$,

$d = 2.609$, and

$g = 4.1 \times 10^{-5}$.

The correlation coefficient for this model is 0.939.

The predictive accuracy of the selected model (Eqn. 5-1) is illustrated in Figure 5-3. The predicted emission level E at four hours is plotted as a function of the measured emission levels. If the correlation was perfectly accurate, all the points would fall on the solid line shown in Figure 5-3. The volatility and loading are the dominant parameters, but most of the modeling efforts have indicated a small but persistent effect of humidity. One feature of this model which does appear to be inconsistent is the factor g. Thus, this model predicts a low level of emissions (4.1×10^{-5} lb/ft^2) at zero loading. The level is very small, however, and the presence of this constant may simply be the result of the data scatter. It may also reflect the fact that soil D-8 did, at times, exhibit some emission activity before any sludge was spread.

The results of this study apply within the following ranges of parameters:

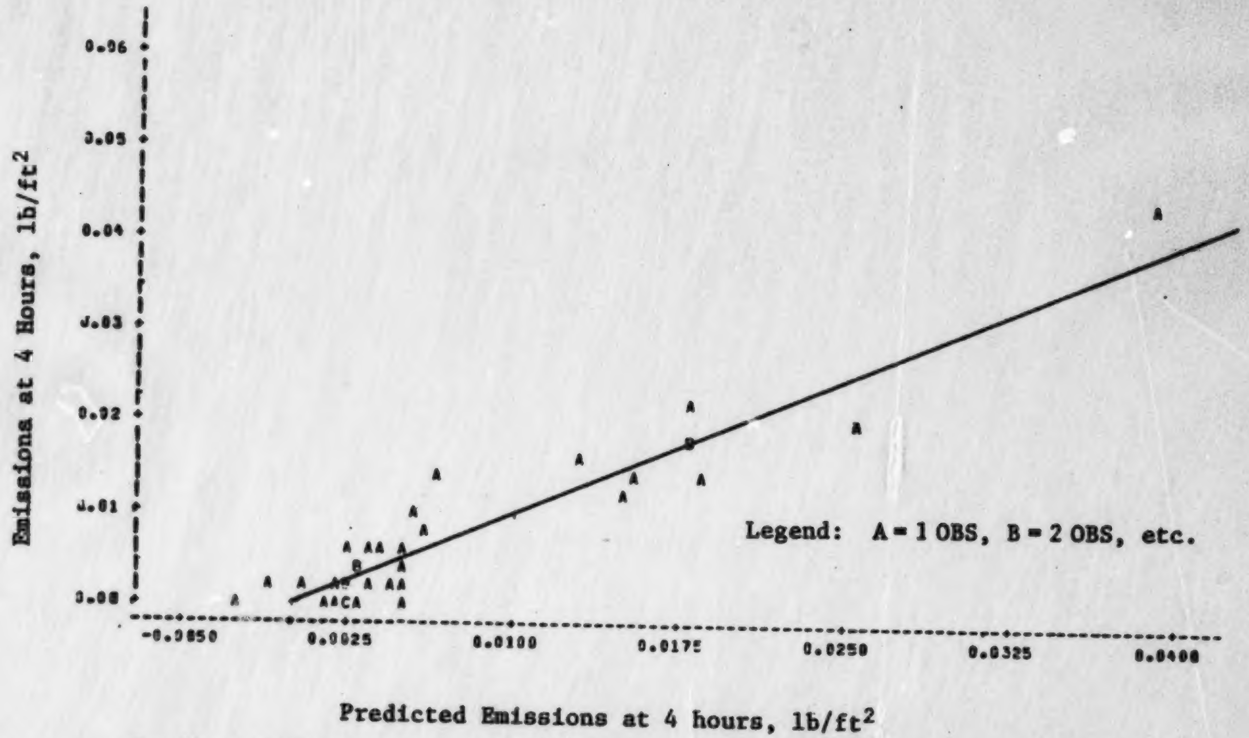
$0 \leq L \leq 1.25$

$0 \leq V \leq 820$

$30 \leq H \leq 70$

$5 \leq M \leq 25$ M = moisture content of soil

An alternate response variable, E_2 (the emission level at seven hours after spreading) was also tested with the preferred model. It showed a correlation coefficient of 0.97 indicating that conclusions developed with E readily apply to E_2.



Predictive Model: $E = 6.94 \times 10^{-14}\ VL\ [H(100-H)]^{2.61} + 4.1 \times 10^{-5}$

Figure 5-3. Comparison of Experimental and Predicted Values of E, Emission Levels at Four Hours from Spreading

A great deal of care is necessary in the interpretation and use of the model developed in this study (Eqn. 5-1). The model is useful in demonstrating the relative importance and interrelationship of the VOC emissions, sludge volatility, sludge loading, and humidity. At the same time, other variables which were initially considered to be influential, such as soil type and soil moisture, appear to be insignificant in their effect on the level of VOC emissions. It must be kept in mind, however, that the model developed in this study is a preliminary one, and it is based on limited and incomplete data. Above all, the model is not a rate model. It simply predicts the cumulative VOC emissions during the first four hours after spreading the sludge (without any tilling). The apparent accuracy of this preliminary model provides some hope for the development of a rate model in the future. Much additional study and data will be necessary, however, before a valid rate model can be developed with any degree of confidence. Furthermore, it should be pointed out that there has not been any field verification of the laboratory apparatus as an accurate simulation of full-scale land treatment activities.

An attempt was made to develop a model from the 30-minute emission levels of both the Phase I and Phase II studies. It was unsuccessful due to the data scatter of the 30-minute measurements. Another factor was the very considerable difference in volatilities of the sludges used in phase I and phase II. The volatility of the principal sludge used in the phase I study was greater by several orders of magnitude than the volatilities of any of the sludges tested in phase II.

5.2 EFFECT OF ELAPSED TIME ON VOC EMISSIONS

In the phase I program, the effect of elapsed time (after the sludge application) on the VOC emissions was quite dramatic. However, the volatilities of the sludges tested in this current study are less (by several orders of magnitude) than those of the phase I tests. Thus, the peak hydrocarbon concentrations normally seen soon after application were not as high as those observed in phase I testing. However, the general form of the hydrocarbon concentration-elapsed time curve is similar. This is illustrated in Figure 5-4 for Run No. 12.

In this test, approximately 0.6 pounds of sludge SL-11 was applied to soil D-1. The concentration rose almost immediately to a peak detected value of 24 ppmv. The concentration then declined in an exponential manner over the next four hours, to levels in the range of 2 ppmv. Approximately 1.8 percent of the applied oil was vaporized in this four-hour period (see Table 4-8). This pattern was typical of those seen when applying sludge SL-11, the most volatile of the sludges tested in phase II.

A somewhat unexpected pattern of emissions as a function of elapsed time was observed in many of the tests with other less volatile sludges. Examples of this pattern are shown in Figure 5-5 (Run No. 13) and 5-6 (Run No. 35). The relatively high peak concentration is initially seen immediately after sludge application. This is followed by an initial decline in concentration, but then the concentration increases with time. In the case of Run 13, a maximum concentration of about 12.7 ppmv was observed. This was slightly higher than the initial peak concentration of about 11.2 ppmv. After the second maximum concentration was reached, the concentration declined exponentially with time.

The same phenomenon is illustrated for Run No. 35 in Figure 5-6. The concentrations are much lower than those of Run No. 13, but a sharp peak in the concentration was observed at about 220 minutes after the sludge application. The concentration level in the air over the soil appeared to be relatively constant at about 0.2 ppmv both before and after the peak concentration occurred.

This behavior was observed in a majority of the test runs with the less volatile sludges. It was not a random artifact, but was, in fact, reproducible. A definitive explanation for the observed behavior has not yet been proposed.

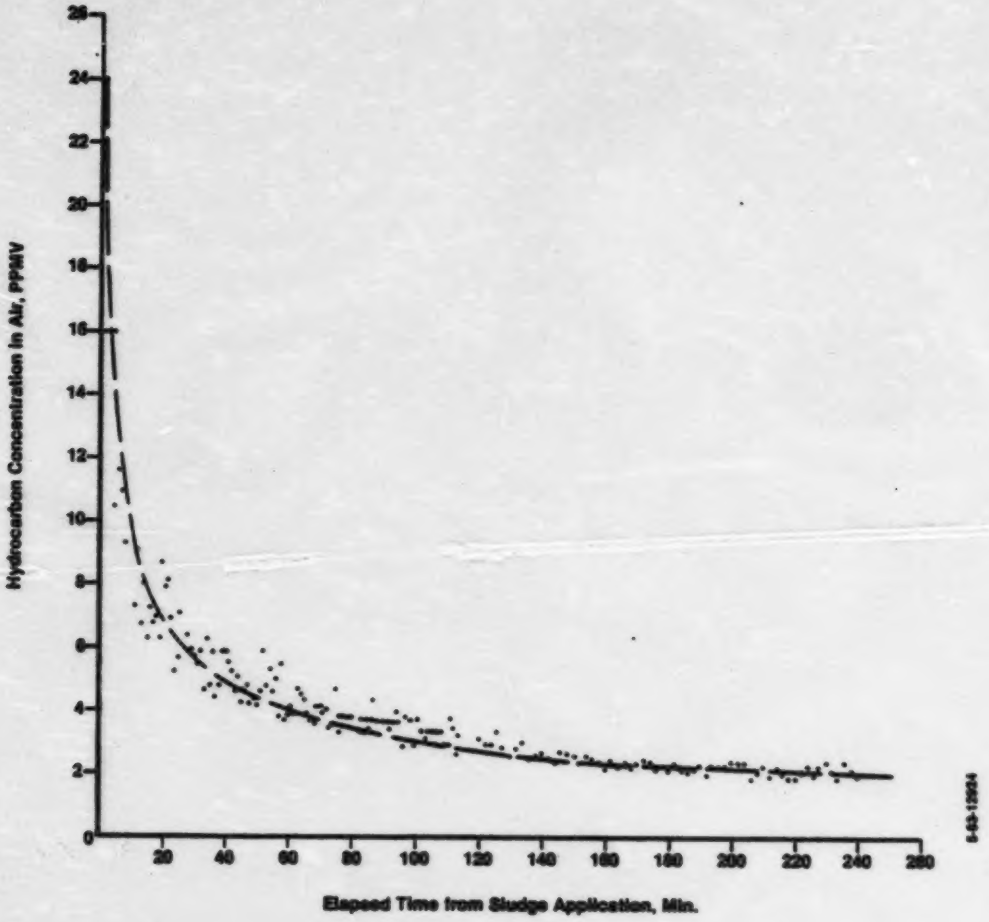


Figure 5-4. Hydrocarbon Concentration in Air During Run 12 (0.6 lb of SL-11 on Soil D-1)

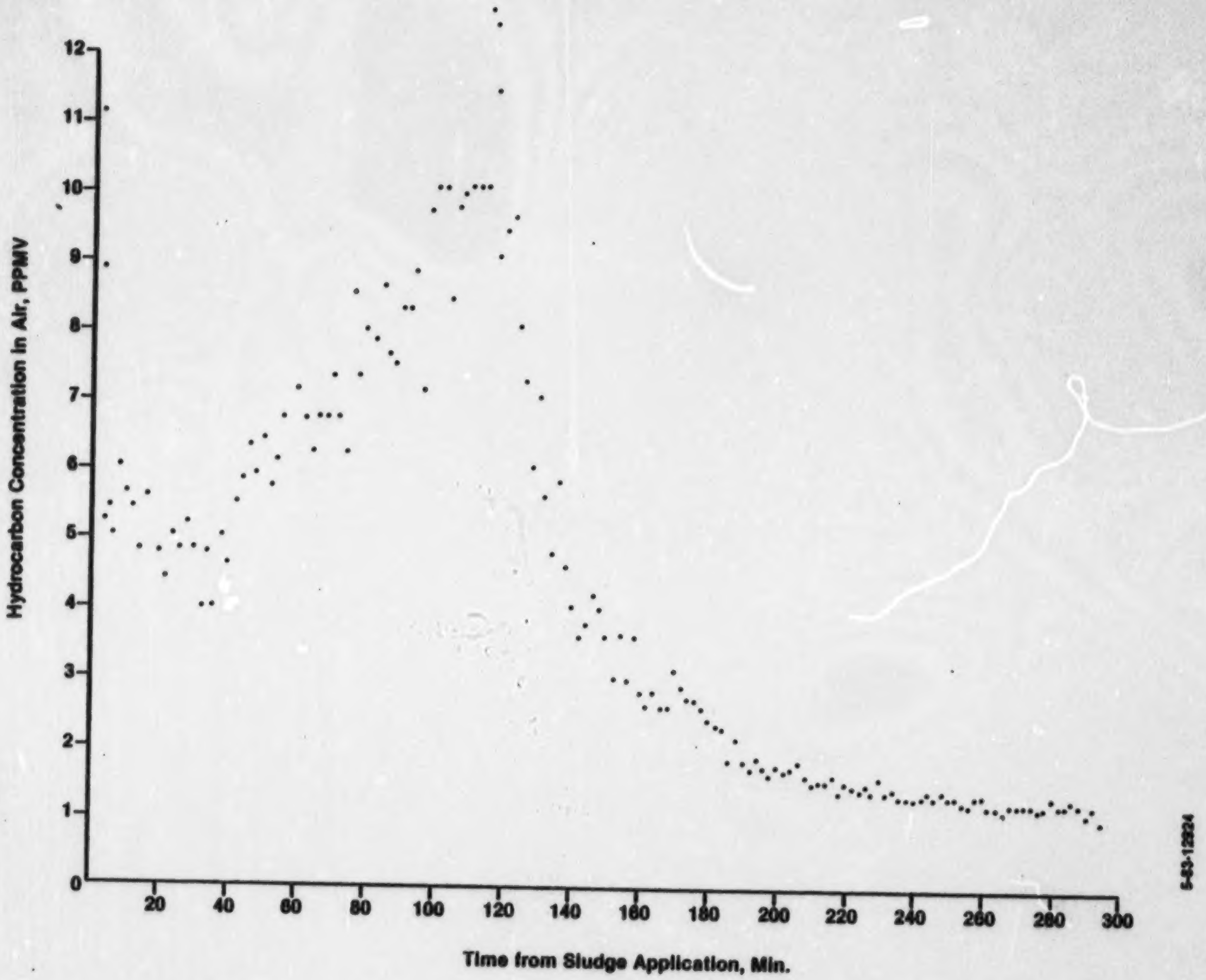


Figure 5-5. Hydrocarbon Concentration in Air During Run 13 (2.3 lbs of SL-11 on Soil D-1)

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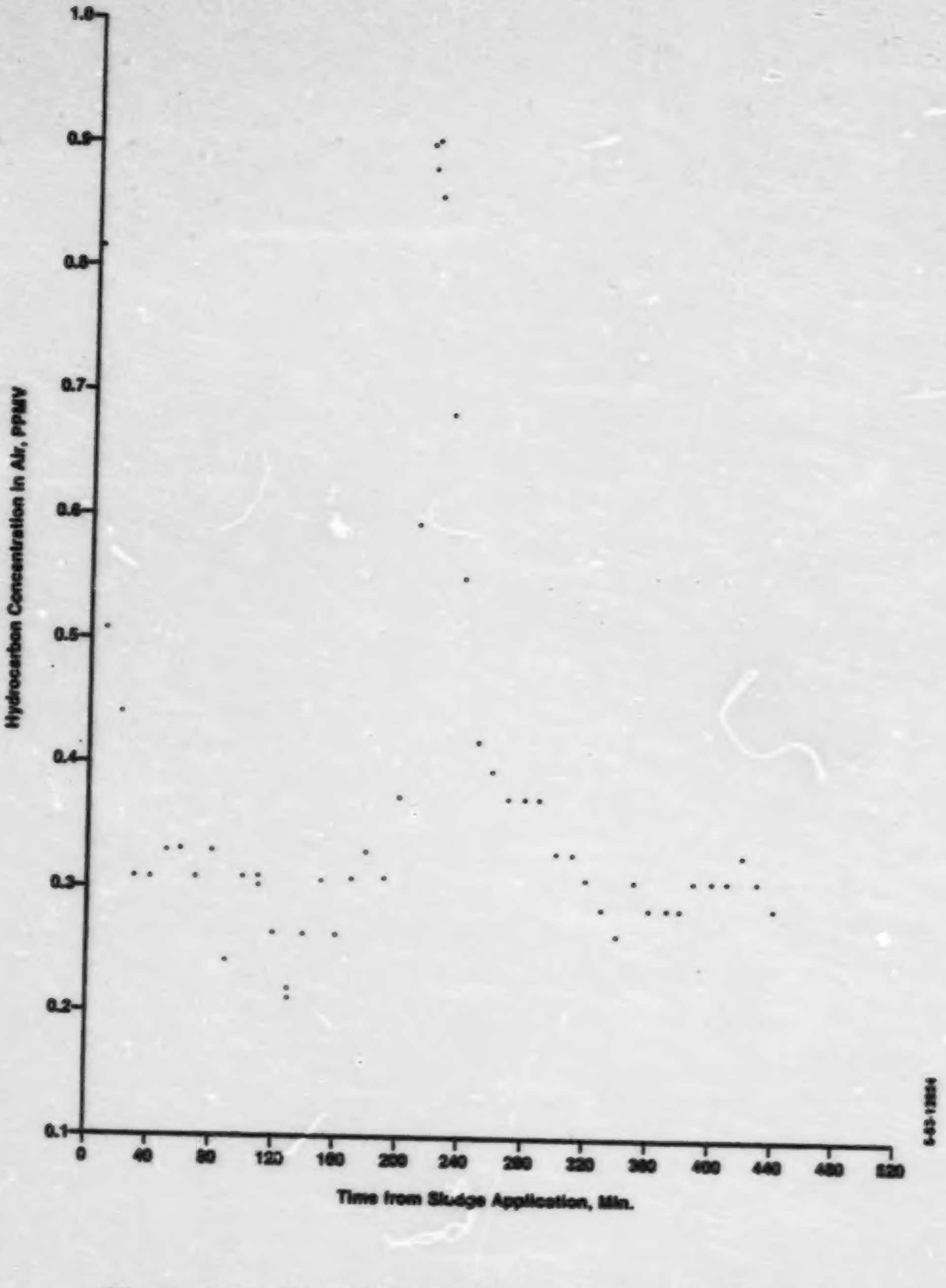

Figure 5-6. Hydrocarbon Concentration in Air During Run 35 (1.06 lbs SL-12 on Soil D-8)

The fraction of applied oil which was vaporized during the tests ranged from 0 to 9.2 percent at seven hours after sludge application. The vaporization behavior is summarized in Table 5-3. The overall average percentage of vaporized oil was 2.0 percent and 3.4 percent at four and seven hours, respectively, after sludge application. Also shown in Table 5-4 is the estimated amount of hydrocarbon (oil) vaporized during the four-hour stripping test.

In several cases, the soil chamber containing soil and applied sludge was removed from the land treatment simulation apparatus. The soil chamber was then placed under a hood for periods up to two weeks. After the soil/sludge mixture had been exposed to ambient conditions for these longer time periods, the soil chamber was placed back in the simulation apparatus, and the emissions were measured. The results of one such study are summarized in Table 5-4.

The average hydrocarbon concentration in the air from the soil chamber is shown for the last hour of the initial test period of about eight hours. The VOC concentrations are also shown as they were measured after the soil chamber had been exposed to ambient condition for about 312 hours. The concentrations were measured over a four-hour period, and as expected, they were considerably lower after the long-term exposure. The concentration decreased from about 2 ppmv at the end of eight hours to about 0.1 ppmv after the long-term exposure. The emission behavior of the land-treated soil during the long-term exposure was not monitored. However, the concentrations are shown graphically in Figure 5-7. The emission level appears to be decreasing exponentially during the first seven to eight hours of the test period. Because of the low concentrations present after the long-term exposure, the pattern of decline (if present) is not evident. However, it does appear that there was some small decline in concentration over the four-hour monitoring period.

It should be noted, however, that the detection limit of the hydrocarbon monitor is in the range of 0.1 ppmv. Additionally, at this low level, the source of the hydrocarbons is uncertain. They may be emitted from the applied

TABLE 5-3. VAPORIZATION OF OILY SLUDGE

Sludge ID	Amount of Oil Sludge Vaporized, % of Applied Oil[a]						Oil Vaporized During 4-Hour Stripping Test, % of Oil in Sludge
	4 Hours After Application			6 Hours After Application			
	Average	Maximum	Minimum	Average	Maximum	Minimum	
SL-11	3.3	6.0	0.6	4.1	8.4	0.6	46.6
SL-12	0.5	1.4	0.06	0.9	1.8	0.15	6.0
SL-13	1.9	4.1	0.15	4.0	8.4	0.4	18.4
SL-14	1.8	5.9	0.0	3.6	9.2	0.0	12.2
Overall	2.0			3.4			

[a] Applied oil amount estimated from results of centrifugation tests

TABLE 5-4. AVERAGE HC CONCENTRATION IN AIR AFTER EXPOSURE OF LANDTREATED SOIL TO AMBIENT CONDITIONS FOR AN EXTENDED PERIOD (Run 41)

Time After Sludge Application, Min.	Average HC Concentration in Air, PPMV
420-429	2.33
430-439	2.26
440-449	2.18
450-459	2.12
460-469	1.89
470-472	2.07
Time After Exposing Landtreated Soil to Ambient Conditions for ∿ 312 Hours	
0-30 min.	0.159
31-60	0.144
61-90	0.153
91-120	0.096
121-150	0.079
151-180	0.089
181-210	0.092
211-240	0.110

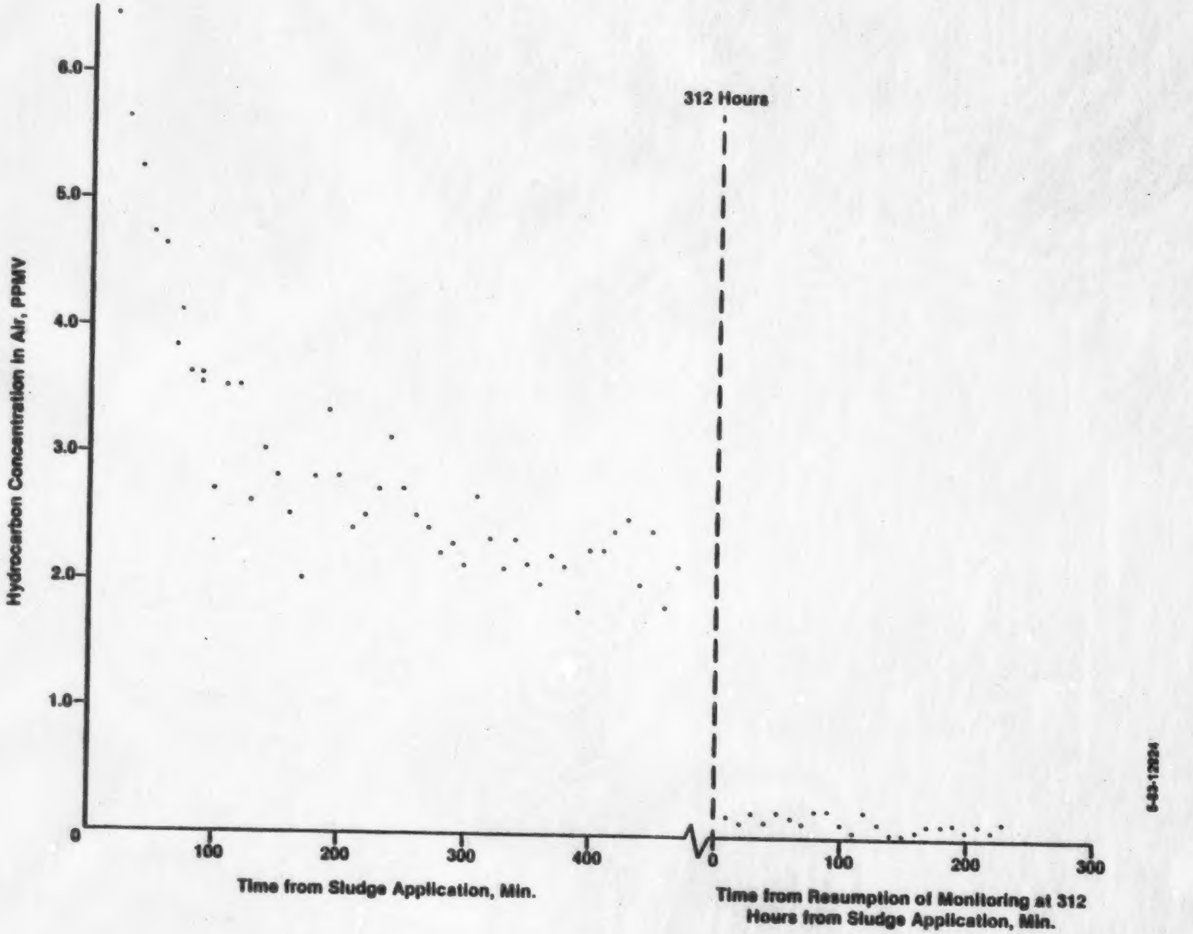

Figure 5-7. Hydrocarbon Concentration in Air During Run No. 41

sludge, or the soil itself may be a source of some hydrocarbon vapors from past field applications. Even background levels of hydrocarbon in the ambient air could be contributing to the apparent low emission level. Thus, it is difficult to accurately ascertain the contribution of the applied sludge to the long-term emission behavior of the system when the hydrocarbon concentrations are at such low levels.

In two cases, the soil was tilled after long-term exposures. Results obtained during Run 51 are shown graphically in Figure 5-8. During the last two hours of the initial test period, the emission level appeared to increase at a rather steady pace. After 216 hours at ambient conditions, the emission level, although noticeably lower, appeared to be still present at 0.2 and 0.3 ppmv. It did appear to be declining slightly during the two-hour monitoring period following long-term exposure.

At about two hours after the monitoring was started, the soil was tilled to a depth of about six inches. Not unexpectedly, the hydrocarbon concentration rose almost immediately to a maximum level of about 1.2 ppmv. This diminished very quickly, however, and in about two hours, the concentration of hydrocarbon was at about the same level as that observed prior to tilling. The concentration appeared to remain stable at about 0.20 to 0.25 ppmv for the remaining two hours of monitoring. The hydrocarbons emitted as a result of the tilling operation amounted to about 0.04% of the applied oil.

Other long-term exposure and tilling tests showed basically the same type of behavior.

5.3 COMPOSITION OF EMISSIONS FROM LANDTREATMENT SIMULATIONS

During several of the test runs, samples of the air from the soil chambers were collected in stainless steel canisters. The majority of the samples were collected during the first 30 to 60 minutes of a test. The samples were analyzed using cryogenic GC techniques which permit analysis of volatile

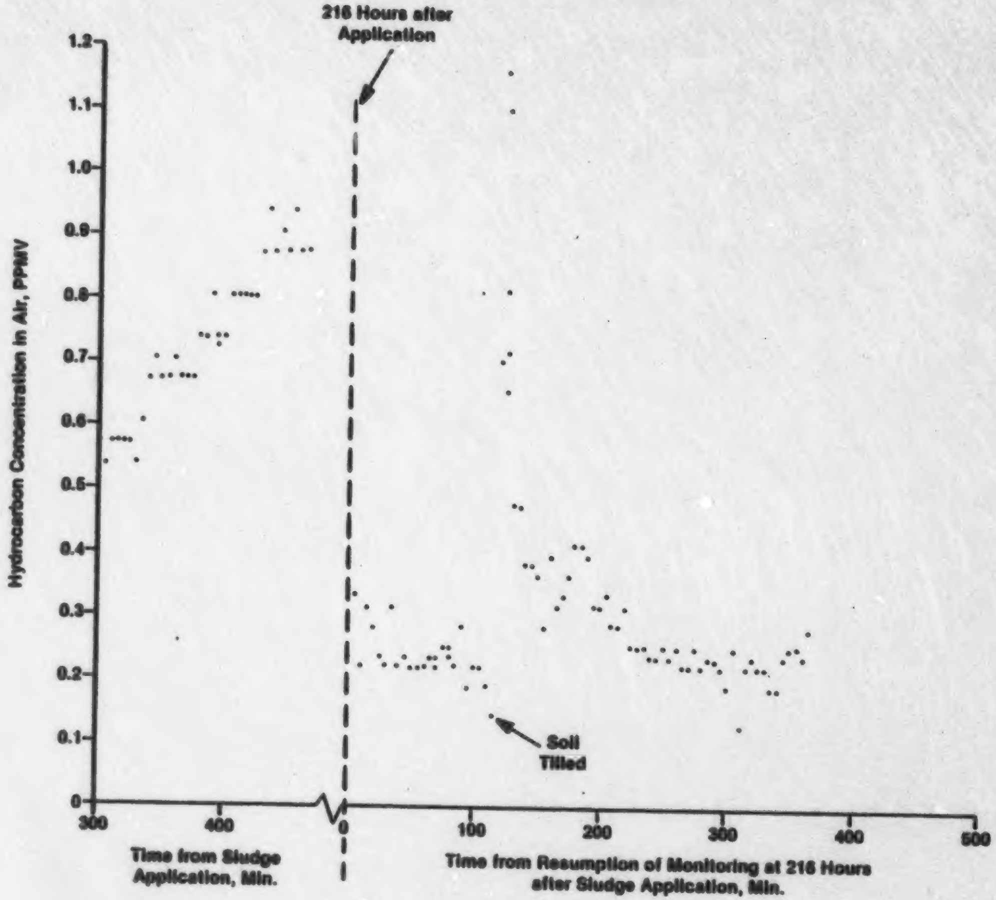

Figure 5-8. Hydrocarbon Concentration in Air During Run No. 51

compounds at very low concentrations. Analyses by GC/MS were not satisfactory, due mainly to the very low concentration levels in the air samples.

Detailed results of the analyses are presented in Appendix D. A summary of some selected component concentrations is given in Tables 5-5 through 5-7. These component concentrations are compared to those determined during analyses of the sludges. The ratio of the component concentrations to some base component (o-xylene or m/p-xylene) is also shown.

In general, the results show that the more volatile components of the sludge are emitted into the air. It appears, from a comparison of the component ratios in the sludge and air, that the more volatile components are present in the air in relatively higher amounts than found in the sludges. A similar result would be expected in comparing a multicomponent liquid composition to the composition of the vapor in equilibrium with the liquid. If a component concentration ratio is higher in the air than in the sludge, the component was preferentially vaporized during the sampling period. In Run 39 (see Table 5-7), for example, the ratio of benzene to m/p-xylene is 0.17 in the sludge, and 0.52 in the air above the landtreated sludge. Relative to the m/p-xylene, then, a greater fraction of the benzene was vaporized than was the m/p-xylene. Although there is considerable scatter in the results, it appears that generally compounds lighter than C_3-benzenes are preferentially volatilized, compared to the heavier compounds (detected in the air samples).

There are some differences between the hydrocarbon concentration observed during the test periods and the total concentration determined from the samples taken in canisters. These are summarized in Table 5-8. In almost all cases, however, the concentrations are within the same order of magnitude. The differences in concentrations are not unexpected given the level of hydrocarbon concentrations, variability of the emissions during the initial emission period, and the sensitivity of the hydrocarbon analyzer at these low levels.

TABLE 5-5. COMPOSITION OF AIR FROM SOIL CHAMBER DURING TESTS WITH SLUDGE SL-11

Compound	Sludge Sample			Run 41 Composition of Emissions	
	Sludge Composition, µg/gm	Relative Concentration, wt %	Weight Ratio, Relative to o-Xylene	SL-11 on D-7 Concentration,[a] ppbv-c	Weight Ratio Relative to o-Xylene
Benzene	540	8.9	1.64	0.240	0.17
Toluene	1,700	27.9	5.15	1.481	1.21
m/p-Xylene	700	11.5	2.12	2.382	2.24
o-Xylene	330	5.4	1.00	1.062	1.00
C_3-Benzene	1,100	18.0	6.03	2.366	2.53
C_3- Benzene	890	14.6			
Naphthalene	230	3.8	0.70	--	--
Anthr./Phen.	150	2.5	0.45	--	--
C_9-H.C. (alkane)	130	2.1	0.39	2.036	2.31
C_{12}-H.C. (alkane)	140	2.3	0.42	--	--
C_{17}-H.C. (alkane)	84	1.4	0.25	--	--
C_{17}-H.C. (alkane) (pristine)	66	1.1	0.20	--	--
C_{19}-H.C.	31	0.5	0.09	--	--
C_{20}-H.C.	2	0.0	0.01	--	--
TOTAL	6,093	100			

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[a] A dashed line in this column indicates that the compound was not detected in the air sample.

TABLE 5-6. COMPOSITION OF AIR FROM SOIL CHAMBER DURING TEST WITH SLUDGE SL-13

	Sludge Samples			Composition of Emissions, Run 43 After Tilling	
Compound	Sludge Composition, µg/gm	Relative Composition, wt %	Weight Ratio, Relative to m/p-Xylene	ppbv-c[a]	Weight Ratio, Relative to m/p-Xylene
Benzene	18	0.6	0.16	12	0.44
Toluene	98	3.4	0.89	32	1.39
m/p-Xylene	110	3.8	1.00	20	1.00
o-Xylene	50	1.7	0.45	--	--
C_3-Benzene	400	13.7	7.27	58	3.3
C_3-Benzene	400	13.7			
Naphthalene	350	12.0	3.18	--	--
Anthr./Phen.	1,100	37.8	10.0	--	--
C_9-H.C. (alkane)	14	0.5	0.13	21	1.27
C_{12}-H.C. (alkane)	210	7.2	1.91	41	3.3
C_{17}-H.C. (alkane)	84	2.9	0.76	--	--
C_{17}-H.C. (alkane) (pristane)	24	0.8	0.22	--	--
C_{19}-H.C.	40	1.4	0.36	--	--
C_{20}-H.C.	16	0.5	0.15	--	--
	2,914				

[a] Dashed line indicates that the compound was not detected in the air sample.

TABLE 5-7. COMPOSITION OF AIR FROM SOIL CHAMBER DURING TESTS WITH SLUDGE SL-14

	Concentration in Sludge			Run 29: SL-14 on D-1 Concentration in Air[a]		Run 29: SL-14 on D-1 Concentration in Air[a]		Run 39: SL-14 on D-1 Concentration in Air[a]		Run 42: SL-14 on D-1 Concentration in Air[a]	
	μg/gm	Weight Percent	Weight Ratio, Relative to m/p-Xylene	ppbv-c	Weight Ratio, Relative to m/p-Xylene	ppbv-c	Weight Ratio, Relative to m/p-Xylene	ppbv-c	Weight Ratio, Relative to m/p-Xylene	ppvb-c	Weight Ratio, Relative to m/p-Xylene
Benzene	5	0.6	0.17	204	2.44	72	0.73	21	0.52	53	0.61
Toluene	14	1.8	0.47	166	2.83	200	2.38	72	2.08	94	1.27
m/p-Xylene	30	3.8	1.00	51	1.00	73	1.00	30	1.00	64	1.00
o-Xylene	16	2.0	0.53	-	-	-	-	10	0.33	13	0.20
C_3-Benzene	160	20.4	5.33	363	7.99	39	0.60	34	1.28	94	1.66
C_3-Benzene	140	17.8	4.67								
Naphthalene	64	8.1	2.13	185	4.38	52	0.86	-	-	-	-
Anthr./Phen.	92	11.7	3.07	-	-	-	-	-	-	-	-
C_9-H.C. (alkane)	36	4.6	1.20	19	0.45	-	-	-	-	53	1.00
C_{12}-H.C. (alkane)	120	15.2	4.00	-	-	-	-	-	-	-	-
C_{17}-H.C. (alkane)	68	8.6	2.27	-	-	-	-	-	-	-	-
C_{17}-H.C. (alkane) (pristane)											
C_{19}-H.C.	28	3.6	0.93	-	-	-	-	-	-	-	-
C_{20}-H.C.	14	1.8	0.47	-	-	-	-	-	-	-	-
	787										
Sampling Time Period:				Sample collected for 60 minutes at start of run		Sample collected for 60 minutes at 4 hours after run start		Sample collected for 1 hour at start of run		Sample collected for 30 minutes at start of run	

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[a] Dashed line indicates that the compound was not detected in the air sample.

TABLE 5-8. AVER[illegible] CONCENTRATIONS AND CONCENTRATIONS OF AI[illegible]

Run Number	Average Monitored Hydrocarbon Concentration, ppmv (as hexane)		Canister Concentration	
	First 30 Minutes	First Hour	ppmv-c	ppmv (as hexane)
29	0.101	0.06	2.58	0.43
29	--	--	1.26	0.21
39	1.17	1.22	2.22	0.37
41	8.2	6.7	30.42	5.07
42	0.42	0.23	2.54	0.42
43	3.73	2.43	1.35	0.23
51	0.54	0.42	8.90	1.48
51	0.54	0.42	1.83	0.31

5.4 COMPARISON OF MEASURED AND PREDICTED RATES

In one experimental run, No. 29, a sample of the air from the soil chamber was collected over a one-hour period, starting four hours after the sludge was applied. The air sample was analyzed for some individual volatile compounds. The average emission rate of the individual compounds during this one hour period were calculated, and these were compared to the emission rates calculated from the mathematical model proposed by Thibodeaux and Hwang (3).

The proposed model is shown in Table 5-9. It can be applied after the sludge has soaked into the soil.

The experimental and predicted rates are given in Table 5-10. Relatively close agreement was obtained for three of the four compounds examined. A considerable difference between the experimental and predicted rates was observed for the m/p-xylene.

It is not possible to develop from the results shown here, any definitive conclusions regarding the accuracy of the Thibodeaux-Hwang Model. The data are too limited, and represent a single experimental value. Nevertheless, the results are encouraging and provide some incentive to continue validation of the mathematical approach developed by Thibodeaux and Hwang as a method for predicting single component emissions.

An example calculation is shown in Appendix B.

TABLE 5-9. PROPOSED MATHEMATICAL MODEL

Model: Thibodeaux-Hwang (3)

Disposal Method: Landtreatment

Type of Model: Predictive

Basis: Emission rate is controlled by diffusion of vapor through the air-filled pores of the landtreated soil.

Form:

$$q_i = \frac{D_{ei}\, C_{ig}}{\left[h_s^2 + \frac{2\, D_{ei}\, t\, A\, (h_p - h_s) C_{ig}}{M_{io}}\right]^{\frac{1}{2}}}$$

and

$$C_{ig} = \left[\frac{H_c}{1 + H_c\, \frac{D_{ei}\, Z_o}{D_{wi}\, A_s\, f(\bar{y})}}\right] C_{io}$$

where

q_i = flux of component i from the soil surface, g/cm^2-sec

D_{ei} = effective diffusivity of component i in the air-filled soil pore spaces, cm^2/s

C_{ig} = effective wet zone pore space concentration of component i, g/cm^3

h_s = depth of subsurface injection (if applicable), cm

h_p = depth of soil contaminated or wetted with landtreated waste, cm

t = time after application, sec

A = surface area over which waste is applied, cm^2

M_{io} = initial mass of component i incorporated into the zone $(h_p - h_s)$, g

H_c = Henry's-law constant in concentration form, cm^3 oil/cm^3 air

Z_o = oil layer diffusion length, cm

D_{wi} = effective diffusivity of species i in the oil, cm^2/s

A_s = interfacial area per unit volume of soil for the oily waste, cm^2/cm^3

$f(\bar{y}) = \bar{y}\,(h_p - \bar{y})$, accounts for the lengthening dry zone

$\bar{y}$ = height of wetted soil remaining after partial drying, cm

TABLE 5-10. COMPARISON OF PREDICTED AND MEASURED EMISSION RATES OF INDIVIDUAL COMPONENTS DURING EXPERIMENT RUN 29

	Emission Rate, gr/cm^2-sec	
Compound	Experimental	Predicted
Benzene	1.77×10^{-9}	1.26×10^{-9}
Toluene	4.87×10^{-9}	3.66×10^{-9}
m/p-xylene	1.81×10^{-9}	9.02×10^{-9}
naphthalene	1.18×10^{-9}	2.45×10^{-9}

SECTION 6

RECOMMENDATIONS

The mechanisms involved in landtreatment and the formation of VOC emissions from these operations are extremely complex. The results of the two phases of this study have indicated the presence of measurable VOC emissions from the landtreatment of oily sludges. At the same time, several variables have been identified as having a measureable effect on the level of VOC emissions. All of this work has so far been done in the laboratory. Laboratory simulations have substantial advantages in both cost and variable control over field studies. However, at some point, the validity of the laboratory simulations must be proven by comparing laboratory results with field study observations.

It seems that this point has been reached. Before any further substantial laboratory studies are initiated, field validation of the laboratory simulations is recommended. This could be accomplished, for example, with simultaneous field and laboratory runs with the same sludges, soils, atmospheric conditions, etc.

After the laboratory simulation technique has been validated, additional laboratory studies could be performed to accomplish some or all of the following.

- An evaluation of the significance of the VOC emissions from landtreatment relative to other sources to assess whether this source warrants further study.
- An evaluation of the effect of air and soil temperature on the level of VOC emissions.

- A determination of the rate of biodegradation experienced during landtreatment, and the effect of variables such as sludge composition, soil type/temperature, and nutrients on the rate.

- Long-term studies to develop a rate expression that could be used to predict emissions from landtreatment operations as a function of time.

- An evaluation of existing mathematical models for predicting landtreatment emissions. The existing proposed models apply only to single components, and they have not been validated. A multicomponent model, using easily-obtained data, is needed.

- An evaluation and development of methods to reduce VOC emissions from landtreatment.

SECTION 7

REFERENCES

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2. Cox, R. D., and R. D. Earp. Determination of Trace Level Organics in Ambient Air by High-Resolution Gas Chromatography with Simulataneous Photoionization and Flame Ionization Detection. Analytical Chemistry 54 (13): 2266-2270. November 1982.

3. Thibodeaux, L. J. and S. T. Hwang. Landfarming of Petroleum Wastes--Modeling the Air Emission Problem. Environmental Progress 2 (2): 42, February 1982.

APPENDIX A

REFINERY QUESTIONNAIRE

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INTRODUCTION

Radian Corporation, under contract with the American Petroleum Institute, is conducting an investigation of atmospheric hydrocarbon emissions from landtreatment of refinery oily sludges. This study will involve laboratory simulation of sludge landtreatment to assess the effects of various parameters on the atmospheric emission rate from landtreatment. Radian will use sludges and soils obtained from U.S. petroleum refineries in the simulation studies.

The American Petroleum Institute has identified several candidate refineries for obtaining sludge and soil samples. Because of contract funds limitations, Radian Corporation will not be able to visit any refinery facilities to obtain samples. Therefore, each candidate refinery is being asked to ship sludge and soil samples to Radian Corporation. The following pages include a summary of sampling/shipping procedures and several questions about the sludge and soil samples.

The reason that detailed questions are needed is to permit broader application of the results of the study. For example, a refinery could estimate emissions from landtreatment of sludges by determining which of the tested sludges and soils were similar to that refinery's sludge and soil, based on the characteristics listed in the questionnaire. In addition to specific questions about each sample, several general questions are included. This information will be used to make an estimate of the relative magnitude of atmospheric emissions from landtreatment at all U.S. refineries. It is recognized that some of the information requested may be difficult or impossible to determine in all cases. Please provide the most complete information that can be obtained with a reasonable amount of effort.

Any questions about samples, procedures, or questionnaires can be directed to Russell Honerkamp or Bob Wetherold at Radian Corporation (Austin, Texas, 512/454-4797) or to J. Eldon Rucker of the American Petroleum Institute (Washington, D.C.). (202) 457-7087.

GENERAL QUESTIONS

Refinery name/location:

Refinery capacity/classification*:

Sludge production rates: (also list any known sludge characteristics, e.g., % water, % oil, % solids, etc.)

Tank bottoms (list separately if individual rates are known)

Separators (list separately if individual rates are known)

Biological oxidation

Others (describe)

*Topping, Cracking, Petrochemical, Lube, or Integrated

SAMPLE REQUIREMENTS

Size: 5 gallons

Container: Polypropylene bag liner in metal bucket with crimp type lid. Expel all air from the bag prior to sealing the sample in the bag.

Sampling procedure: Any method that will yield a sample respresentative of normal operation. Try to minimize exposure of sample to air, or any other action or agents, that could alter the sample.

Label: Sample I.D. number to correspond with questionnaire.

GENERAL QUESTIONS (continued)

SHIPPING REQUIREMENTS

Label: Hazardous Substance (Liquid or Solid) N.O.S. NA9188

Ship via: Motor freight

Ship to: Radian Corporation
Attention: John Randall
8501 Mo-Pac Boulevard
Austin, TX 78758

SOIL SAMPLE

Sample I.D. Number:

Soil classification (e.g., sand, clay, loam, etc.):

Previous use of soil:
- ☐ Undeveloped
- ☐ Farming
- ☐ Residential/Commercial
- ☐ Industrial (describe)
- ☐ Landtreatment

Present use of soil:

(Note: the ideal soil sample should come from an active landtreatment facility. The soil should be from an area previously used, ideally from an area scheduled for sludge application in the near future.)

Description of landtreatment facility

Physical description (e.g., alternating vegetation strips, size of area, type of vegetation, etc.):

Application method:

Fertilizer applied (rate):

pH control:

Tilling Schedule:

Sample Origin

Length of service for sample soil:

Number of applications to sample soil:

Description of sludge(s) applied:

Application rate/frequency:

Method of sampling (e.g., single point, random multi-point, grid composite, etc.): (Note: Samples should be obtained to depth of tilling only).

SLUDGE SAMPLE

Sample I.D. Number:

Sludge origin: (Note: Sludge should be "as applied" to landtreatment. If sludges from several sources are mixed, estimate % of each type in the combined sample.)

☐ Tank bottoms; tank fluid

☐ Separator sludge

Type of separator (API, DAF, centrifuge, etc.):

Source of separator influent (process units):

Sludge removal method (batch, continuous):

☐ Biological oxidation sludge

Source of influent:

☐ Other (explain):

Sludge disposition

What treatment applied to sludge before disposal? (de-watering, weathering, stripping, etc.)

What is present disposal for this sludge?

Is this sludge presently deemed landtreatable? (If not, give reasons.)

If this sludge is disposed of by landtreatment:

Application rate (pounds or gallons of sludge, as sampled, per area of land):

Application frequency:

Sludge temperature (ambient/heated):

Application method:

Months of year when applied:

Tillage schedule:

APPENDIX B

SAMPLE CALCULATIONS OF EMISSION RATES

SAMPLE CALCULATIONS USING THIBODEAUX-HWANG MODEL FOR PREDICTING ATMOSPHERIC EMISSIONS

Equations

$$q_i = \frac{D_{ei}\ C_{ig}}{\left[h_s^2 + \frac{2\ D_{ei}\ t\ A\ (h_p - h_s)\ C_{ig}}{M_{io}}\right]}$$

and $$C_{ig} = \left[\frac{H_c}{1 + H_e \frac{6\ D_{ei}\ Z_o}{D_{wi}\ A_s\ (h_p^2 - h_p h_s - Z h_s^2)}}\right] C_{iwo}$$

Conditions

Run No. = 29 @ 4-5 hours from application

Air/Soil Temperature = 90°F

Benzene Concentration in Sludge = 5mg/g

Benzene Concentration in Air = 82 ppbvc

= 12 ppbv as benzene

Variables

D_{ei} = effective diffusivity of component i in the air-filled soil pore, 8.98×10^{-2} cm^2/sec

h_s = depth of subsurface injection, o cm

t = elapsed time at measurement, 4.5 hours, avg (1.62×10^4 sec)

A = surface area of disposal, 1 ft^2 (929 cm^2)

h_p = depth of soil penetration by sludge, 4 inches (10.2 cm)

M_{io} = initial amount of component (benzene) applied to landfarm area,
= 2.13)lb/ft^2) x 1.0 (ft^2) x 454 (g/lb) x 5 x 10^{-6} (gr/gr)
= 4.84×10^{-3} g benzene

Z_o = oil layer diffusion length (assumed film form)

$$= \frac{\text{(particle diameter) (particle density)}}{6 \times \text{(waste density)}}$$

D_{wi} = diffusivity of component (benzene) in waste (assumed to be effectively water)

$= 0.86 \times 10^{-5}\ \text{cm}^2/\text{sec}$

A_s = interfacial area per unit volume of soil for the oily waste, cm^2/cm^3

= 6/particle diameter

$= 6/0.0075 = 800\ \text{cm}^2$

H_e = Henry's law constant in concentration

$= (\text{Henry's law constant} \times 10^6)\ (1/2.44 \times 10^4)\ (\text{g-mol-cm}^{-3})/P(\text{atm})$

$$= \frac{95.48 \times 10^{-3}\ \text{m}^3\text{-atm/mol})(10^6)(\text{cm}^3/\text{m}^3)}{2.44 \times 10^4 \text{cm}^3/\text{mol} \times 1\ \text{atm}}$$

$= 0.225$

C_{iwo} = initial concentration of component (benzene) at the soil/air interface

= initial concentration of benzene in waste

$= 5 \times 10^{-6}\ \text{g/cm}^3$

Sample Calculations - Predicted Value

$$Cig = \left[\frac{0.225}{1 + 0.225 \times \frac{(6)(8.98 \times 10^{-2})(3.8 \times 10^{-4})}{(0.86 \times 10^{-5})(800)(10.2)^2}}\right] 5 \times 10^{-6}$$

$$= \left[\frac{0.225}{1 + 6.4 \times 10^{-5}}\right] 5 \times 10^{-6}$$

$$= 1.125 \times 10^{-6}\ \text{g/cm}^3$$

$$qi = \frac{(8.98 \times 10^{-2})(1.125 \times 10^{-6})}{\left[\frac{(2)(8.98 \times 10^{-2})(1.62 \times 10^{4})(929)(10.2(1.125 \times 10^{-6}}{4.84 \times 10^{-3}}\right]^{1/2}}$$

$$= 1.26 \times 10^{-9}\ \text{g/cm}^2\text{-sec}$$

Sample Calculations - Experimental Value

$$\text{Air Flow} = 3\ \frac{\text{mile}}{\text{hour}} \times 1610\ \frac{\text{meter}}{\text{mile}} \times 0.0309\ \text{meter}^2\ \text{(cross-sectional area)}$$

$$= 4.15 \times 10^{-2}\ \frac{\text{m}^3}{\text{sec}}\quad (@\ 32°\text{C})$$

$$= 3.94 \times 10^{-2}\ \frac{\text{m}^3}{\text{sec}}\quad (@\ 25°\text{C})$$

$$\text{Benzene Emitted} = 12 \times 10^{-9} \times 3.94 \times 10^{-2} = 4.73 \times 10^{-10}\ \frac{\text{m}^3}{\text{sec-ft}^2}$$

$$= 5.09 \times 10^{-13}\ \frac{\text{m}^3}{\text{sec-cm}^2}$$

$$= \frac{5.09 \times 10^{-13}\ \frac{\text{m}^3}{\text{sec-cm}^2}}{0.224\ \frac{\text{m}^3}{\text{gr-mole}}}$$

$$= 2.27 \times 10^{-11}\ \text{gr/mol/sec-cm}^2$$

$$= 1.77 \times 10^{-9}\ \text{gr/sec-cm}^2$$

APPENDIX C

PHASE I: EXPERIMENTAL CONDITIONS AND RESULTS

NOT REPRODUCIBLE

TABLE C-1. MATRIX OF EXPERIMENTAL CONDITIONS FOR LANDTREATMENT SIMULATION RUNS (PHASE I)

Run No.	Waste Material**	Waste Loading (lb/ft²)***	Soil Type	Soil Moisture (wt%)	Soil/Air Temperature (°F/°F)	Air Velocity (mph)	Relative Humidity (%)	Spreading Mechanism	Remarks
1	Hexane	1.0	None	NA	NA/100	3	Amb*	Pour	
2	Hexane	1.0	S	10.7	120/100	3	Amb*	Surface	
3	Gasoline	1.0	None	NA	NA/100	3	Amb*	Pour	
4	Gasoline	1.0	S	10.7	120/100	3	Amb*	Surface	
5	S1	2.5	None	NA	NA/100	3	Amb*	Pour	
6	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Base case
7	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Repeat of base case
8	S1	2.5	S	10.7	120/100	1	Amb*	Surface	
9	S1	2.5	S	16.7	100/80	3	40	Surface	
10	S1	1.0	S	10.7	120/100	3	Amb*	Surface	
11	S1	1.0	S	10.7	120/100	3	Amb*	Surface	Repeat of Run 10
12	S1	2.5	T	4.7	120/100	3	Amb*	Surface	
13	S1	2.5	S	20.7	120/100	3	Amb*	Surface	
14	S1	2.5	S	10.7	120/100	3	75	Surface	
15	T	2.5	S	10.7	120/100	3	Amb*	Surface	
16	S1	2.5	S	10.7	120/100	3	Amb*	Surface	
17	S1	4.0	S	10.7	120/100	3	Amb*	Surface	
18	S1	0.5	S	10.7	120/100	3	Amb*	Surface	
19	S1	2.5	S	10.7	120/100	3	Amb*	Surface	Heat sludge to 140°F
20	S3	1.0	S	10.7	120/100	3	Amb*	Surface	
21	S3	2.5	S	10.7	120/100	3	Amb*	Surface	
22	S3	4.0	S	10.7	120/100	3	Amb*	Surface	
23	S3	1.0	T	4.7	120/100	3	Amb*	Surface	
24	S3	4.0	T	4.7	120/100	3	Amb*	Surface	
25	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 0.5 lb of gas
26	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 1.5 lb of gas
27	S3	2.5+	S	10.7	120/100	3	Amb*	Surface	Spike sludge with 1.5 lb of H_2O
28	S1	2.5	S	10.7	120/100	3	Amb*	Sub-surface	Till soil after spreading
29	S1	2.5	S	10.7	120/100	3	Amb*	Sub-surface	Use deeper injection

*Amb = ambient humidity was typically 50% at room temperature but measured <<30% at 100°F.

**Sludge S1 = Tank Bottoms

Sludge S3 = API Separator Sludge

Sludge T = API Separator Sludge

***Loading of 2.5 lb/ft² is equivalent to approximately 300 barrels/acre.

TABLE C-2. CHEMICAL COMPOSITION OF SLUDGE AND SOIL SAMPLES (PHASE I)

		Concentration, PPM*				
RT(min)	Compound (M/E)	API separator sludge S3	Tank bottoms S1	API separator sludge T	S Soil	T Soil
9.2	Benzene (78)	1,400	1,800	N.D.	0.0085	0.55
15.2	Toluene (92)	5,600	9,300	0.02	0.0075	0.50
18.1	Ethylbenzene (106)	4,300	5,200	0.46	0.0065	1.8
20.5	M,P-Xylene (106)	15,000	23,000	1.2	0.012	5.5
21.2	O,Xylene (106)	32,000	42,000	0.55	0.016	5.0
23.2	Saturated Hydrocarbon (85)	24,000	4,000	5.0	N.D.	6.5
26.2	Indane (118)	28,000	34,000	9.2	N.D.	1.6
25.4	C_3-Benzene (120)	160,000	220,000	7.9	N.D.	12.0
24.0	Dimethylpentene (98)	1,900	2,200	5.0	N.D.	5.0
24.8	Saturated Hydrocarbon (57)	5,200	6,200	6.6	N.D.	13.0
	TOTAL	277,400	347,700	35.9		

*Compounds with retention times up to 21 minutes were quantitated based on actual response factors and compounds with retention times above 21 minutes were quantitated with a response factor of 1.

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TABLE C-3. RESULTS OF SIMULATION RUNS (PHASE I)

Run No.	Variable[1]	Maximum hydrocarbon concentration (ppm)	Integrated area In 6 Min.	Integrated area in 30 min.	Remarks
1	Pure hexane (false bottom)	>10,000	2,460	7,980	Total area at dryness was 8580
2	Pure hexane	>10,000	3,900	5,500	
3	Gasoline (false bottom)	> 5,000	690	1,810	Total area at zero hydrocarbon concentration was 2400
4	Gasoline	>10,000	1,750	2,470	
5	S1 (false bottom)	400	43	342	
6	Base case	215	21	78	
7	Base case (repeat)	200	22	62	
8	Air velocity decreased to 1 mph	310	57	231	
9	Air/soil temperature decreased	260	23	53	
10	Loading decreased	325	49	143	
11	Loading decreased (repeat of 10)	200	31	136	
12	Soil T used	485	86	230	
13	Moisture in soil increased	> 500	85	263	
14	Moisture in air increased	> 500	68	116	
15	Waste T used	35	1	1	
16	Base Case in a deeper box	350	27	71	
17	Loading increased	425	33	81	
18	Loading decreased drastically	250	31	61	
19	Waste heated before spreading	350	45	74	
20	Waste S3 at low loading	23	4	10	
21	Waste S3 used	15	1.5	5	
22	Waste S3 at high loading	25	4	16	
23	Waste S3 low load on T soil	17	2	5	
24	Waste S3 high load on T soil	34	4	12	
25	Waste S3 with low gas spike	7,000	480	760	
26	Waste S3 with high gas spike	>10,000	760	1,360	
27	Waste S3 cut with water	25	5	8	
28	Sub-surface injection	300	17	114	
28A	Tilling of 28	375	29	68	Tilled 30 min. after spreading
29	Sub-surface deep injection	0	0	0	
29A		225	15	15	Tilled 4 days after spreading
29B		50	3	3	Tilled 6 days after spreading

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[1] Variable changes from the base case conditions of Runs 6 and 7. All other variables remained as in Runs 6 and 7.

TABLE C-4. ESTIMATED EMISSIONS FROM SLUDGE APPLIED TO SOIL IN LANDTREATMENT SIMULATION TESTS (PHASE I)

Run/Sludge	Area 30	Grams volatilized*	Weight Sludge applied, g	% Total Sludge volatilized	Weight Oil applied**	% volatilized	Weight Oil applied, g#	% Oil volatilized
6/S1	78	7.9	1135	0.70	1067	.74	999	.79
7/S1	62	6.3	1135	0.56	1067	.59	999	.63
9/S1	53	5.4	1135	0.48	1067	0.51	999	0.54
10/S1	143	14.5	454	3.2	427	3.4	400	3.6
11/S1	136	13.8	454	3.0	427	3.2	400	3.5
12/S1	230	23.3	1135	2.1	1067	2.2	999	2.3
13/S1	263	26.7	1135	2.4	1067	2.5	999	2.7
14/S1	116	11.8	1135	1.0	1067	1.1	999	1.2
15/T	1	0.10	1135	0.009	114	0.88	110	0.90
16/S1	71	7.2	1135	0.63	1067	.67	999	.72
17/S1	81	8.2	1816	0.45	1707	.48	1590	.52
18/S1	61	6.2	227	2.7	213	2.9	200	3.1
19/S1	74	7.5	1135	0.66	1067	.70	999	.75
20/S3	10	1.0	454	0.22	27.2	3.7	91	1.1
21/S3	5	0.51	1135	0.045	68.1	0.75	227	0.22
22/S3	16	1.6	1816	0.088	109	1.5	363	.44
23/S3	5	.51	454	.11	27.2	1.9	91	.56
24/S3	12	1.2	1816	0.066	109	1.1	363	.33
27/S3	8	.81	1135	0.071	68.1	1.2	227	.36

* Based on Figure D response factor.

** Based on % oil by centrifugation.

# Based on gravimetric oil and grease data.

*** S1 = Tank bottoms
S3 = API separator sludge
T = API separator sludge

APPENDIX D

DETAILED ANALYSES OF AIR SAMPLES COLLECTED DURING EMISSION TESTING

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LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 29 Canister # 2

Sample Description LF-14 ON LF-1 @ 15% MOISTURE

Analysis Date 12 JANUARY 1983 Dilution Factor 0.3295

Analyst RFE TNMHC (ppbv-C) 2574.0

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	527.1	3-METHYL PENTANE	16.9
C_3	331.3	BENZENE	203.8
PROPYNE	27.3	n-HEPTANE	40.8
ISOBUTANE	23.7	TOLUENE	165.7
ACETALDEHYDE	11.7	C_8 ALKANE	97.0
ISOBUTENE + 1-BUTENE	113.5	CHLOROBENZENE	72.8
1,3-BUTADIENE	36.0	m- & p-XYLENE	57.2
n-BUTANE	48.5	C_9 ALKANE	18.8
t-2-BUTENE	19.7	1,2,3-TRIMETHYLBENZENE	363.1
c-2-BUTENE	19.4	NAPHTHALENE	185.0
1-PENTENE	27.5		
2-METHYL-1-~~HE~~BUTENE	39.8		
n-PENTANE	27.1		
ISOPRENE	19.8		
t-2-PENTENE	52.0		
~~C~~ METHYLENE CHLORIDE	11.6		
C_5 ALKANE	21.1		
2-METHYL-2-BUTENE	20.0		
ISOHEXANE	14.0		
t-4METHYL-2-PENTENE	19.7		

NOTE - INTERMITTANT ARC WELDING OVER LABORATORY CAUSED ELECTRONIC NOISE WHICH MAY HAVE RESULTED IN FAULTY INTEGRATION OF SOME PEAKS.

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 29 Canister # 6

Sample Description LF-14 ON LF-1

Analysis Date 12 JANUARY 1983 Dilution Factor 0.3268

Analyst RFE TNMHC (ppbv-C) 1264.1

Compound	Concentration (ppbv-C)	Compound	Concentration
C_3	83.9	1,2,3-TRIMETHYLBENZENE	38.5
ISOBUTANE	33.9	NAPHTHALENE	51.6
ISOBUTENE + 1-BUTENE	35.0		
n-BUTANE	76.7		
ISOPENTANE	14.1		
1-PENTENE	27.2		
n-PENTANE	35.7		
ISOPRENE	13.8		
2-METHYL-2-BUTENE	10.9		
NEOHEXANE	35.4		
3-METHYLPENTANE	41.0		
1-HEXENE	35.1		
n-HEXANE	80.0		
BENZENE	72.1		
C_8 ALKANE	48.3		
2,3,4-TRIMETHYLPENTANE	43.7		
TOLUENE	199.2		
2,3,5-TRIMETHYLHEXANE	170.5		
C_9 ALKANE	53.4		
m & p-XYLENE	72.9		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 30 Canister # 15
Sample Description LF-8 ONLY
Analysis Date 12-JANUARY 1983 Dilution Factor 0.3024
Analyst RFE TNMHC (ppbv-C) 831.6

Compound	Concentration (ppbv-C)	Compound	Concentration
C_3	53.0	NAPHTHALENE	35.4
ISOBUTANE	12.5		
ISOBUTENE + 1-BUTENE	57.0		
n-BUTANE	52.8		
t-2-BUTENE	15.9		
C-2-BUTENE	13.3		
ISOPENTANE	15.7		
1-PENTENE	12.0		
2-METHYL-1-BUTENE	46.7		
n-PENTANE	27.1		
C-2-PENTENE	35.1		
2-METHYL-2-BUTENE	30.4		
3-METHYLPENTANE	22.3		
1-HEXENE	10.8		
n-HEXANE	43.2		
BENZENE	54.2		
2,5-DIMETHYLHEXANE	89.3		
TOLUENE	127.1		
m & p-XYLENE	47.1		
o-ETHYLTOLUENE	29.4		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 31 Canister # 11

Sample Description LF-8 SOIL ONLY (REPEAT) 1ST HOUR

Analysis Date 12-JANUARY 1983 Dilution Factor 0.3657

Analyst REE TNMHC (ppbv-C) 818.8

Compound	Concentration (ppbv-C)	Compound	Concentration
C_3	27.7		
ISOBUTANE	58.6		
n-BUTANE	16.9		
BENZENE	298.9		
C_8 ALKANE	86.4		
TOLUENE	117.4		
o-ETHYLTOLUENE	58.8		
NAPHTHALENE	85.1		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 31 Canister # 7

Sample Description LF-8 SOIL ONLY (REPEAT) 2ND HOUR

Analysis Date 12 JANUARY 1983 Dilution Factor 0.3324

Analyst RFE TNMHC (ppbv-C) 10312

Compound	Concentration (ppbv-C)	Compound	Concentration
C_3	23.5		
n-BUTANE	54.0		
ISOPENTANE	31.2		
n-PENTANE	25.7		
1,1-DICHLOROETHYLENE	113		
NEOHEXANE	15.5		
ISOHEXANE	10.2		
3-METHYLPENTANE	25.1		
n-HEXANE	49 2		
2,4-DIMETHYLPENTANE	375.6		
BENZENE	108.7		
2,5-DIMETHYLHEXANE	110.9		
3,3,4-TRIMETHYLPENTANE	18.9		
TOLUENE	103.1		
2,3,5-TRIMETHYLHEXANE	18.6		
CHLOROBENZENE	29.4		
STYRENE	11.1		
— — —			

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 39 Canister # 7

Sample Description LF-14 ON LF-8 ~6.0 lbs

Analysis Date 19 JANUARY 1983 Dilution Factor 0.2998

Analyst RFE TNMHC (ppbv-C) 2216.7

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	93.8	CHLOROBENZENE	32.4
C_3	48 2	ETHYLBENZENE	11.7
ISOBUTANE	17.0	m&p-XYLENE	29 6
1,3-BUTADIENE	39.3	o-XYLENE	10.2
PROPIONALDEHYDE	23.9	1,3,5-TRIMETHYLBENZENE	34 2
ISOPENTANE	28.8	t-BUTYLBENZENE	11.1
ACETONE	50.5	C_{11} ALKANE	11.9
n-PENTANE	36.0	m-DIETHYLBENZENE	20.5
ISOPRENE	17.2	UNKNOWN C_{10} AROMATIC	14.0
c-2-PENTENE	12.4		
METHYLENE CHLORIDE	1,318.3		
ISOHEXANE	10.4		
3-METHYLPENTANE	10.3		
BUTANONE	12.1		
n-HEXANE	67.0		
1,1,1-TRICHLOROETHANE	14.3		
BENZENE	21.0		
TRICHLOROETHYLENE	13.8		
2,3,4-TRIMETHYLPENTANE	10.3		
TOLUENE	72.2		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 41 Canister # 11
Sample Description LF-11 ON LF-7
Analysis Date 21 JANUARY 1983 Dilution Factor 0.1401
Analyst RFE TNMHC (ppbv-C) 30415.1

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	103.7	C_7 ALKENE	111.5
ISOBUTANE	47.8	C_7 ALKENE	181.8
ISOPENTANE	230.6	2,2,4-TRIMETHYL PENTANE	688.8
DIETHYL ETHER	253.7	n-HEPTANE	585.4
METHYLENE CHLORIDE	208.0	C_8 ALKANE	65.2
NEOHEXANE	114.2	METHYL CYCLOHEXANE	577.4
2,3-DIMETHYL BUTANE	47.9	C_8 ALKANE	82.3
ISOHEXANE	156.1	C_8 ALKANE	92.7
3-METHYL PENTANE	132.3	2,5-DIMETHYL HEXANE	200.8
C_6 ALKANE	36.3	C_8 ALKANE	136.6
n-HEXANE	203.1	C_8 ALKANE	163.9
t-2-HEXENE	40.0	2,3,4-TRIMETHYL PENTANE	214.8
c-2-HEXENE	59.3	TOLUENE	1480.7
1,2-DICHLOROETHANE	198.4	C_8 ALKANE	219.1
1,1,1-TRICHLOROETHANE	135.1	3,5,5-TRIMETHYL HEXANE	596.4
BENZENE	239.5	3-METHYL HEPTANE	830.1
CYCLOHEXANE	118.9	C_8 ALKENE	38.8
2,3-DIMETHYL PENTANE	604.4	2,3,5-TRIMETHYL HEXANE	164.6
3-METHYL HEXANE	233.4	C_9 ALKANE	204.7
C_7 ALKANE	128.2	1-OCTENE	254.8

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 41 Canister # 11
Sample Description LF-11 ON LF-7
Analysis Date 21 JANUARY 1983 Dilution Factor 0.1401
Analyst RFE TNMHC (ppbv-C) 30415.1

Compound	Concentration (ppbv-C)	Compound	Concentration
n-OCTANE	1113.0	n-NONANE	1730.5
C_8 ALKENE	127.2	ISOPROPYLBENZENE	59.9
C-2-OCTENE	56.3	C_{10} ALKANE	340.2
C_9 ALKANE	149.0	C_{10} ALKANE	164.4
C_9 ALKANE	481.9	C_{10} ALKENE	377.0
CHLOROBENZENE	311.7	C_{10} ALKANE	169.3
C_9 ALKENE	345.0	C_{10} ALKANE	361 7
C_9 ALKANE	204.9	n-PROPYLBENZENE	249.9
C_9 SATURATED ORGANIC	136.2	C_{10} ALKENE	240.6
ETHYLBENZENE	489.7	m-ETHYLTOLUENE	859 0
C_9 ALKENE	282.0	135-TRIMETHYLBENZENE	586.7
m&p-XYLENE	2382.4	C_{10} ALKANE	820.9
C_9 SATURATED ORGANIC	100.7	β-PINENE	368.7
C_9 SATURATED ORGANIC	89.4	t-BUTYLBENZENE	944.4
C_9 ALKANE	352.4	124-TRIMETHYLBENZENE	220.6
STYRENE	571.1	C_{10} SATURATED ORGANIC	53.4
O-XYLENE	1062.1	C_{10} AROMATIC	109 7
C_9 ALKANE	457.6	n-DECANE	837 4
1-NONENE	221.5	123-TRIMETHYLBENZENE	331 4
C_9 AROMATIC	57.5	C_{11} SATURATED ORGANIC	48.1

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 41 Canister # 11
Sample Description LF-11 ON LF-7
Analysis Date 21-JANUARY 1983 Dilution Factor 0.1401
Analyst RFE TNMHC (ppbv-C) 3041.5.1

Compound	Concentration (ppbv-C)	Compound	Concentration
INDAN	111.1		
C_{11} SATURATED ORGANIC	76.8		
C_{11} UNSATURATED ORGANIC	233.8		
C_{11} ALKANE	142.2		
C_{11} ALKANE	135.3		
m-DIETHYLBENZENE	128.7		
CHLORINATED ALKANE	160.8		
n-BUTYLBENZENE	105.4		
C_{11} ALKANE	84.5		
C_{11} SATURATED ORGANIC	643		
C_{11} SATURATED ORGANIC	43.7		
C_{11} ALKENE	214.1		
C_{11} ALKENE	125.5		
n-UNDECANE	362.3		
C_{12} AROMATIC	96.6		
C_{12} ALKENE	78.8		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 42 Canister # 2
Sample Description LF-14 ON LF-1
Analysis Date 21 JANUARY 1983 Dilution Factor 0.2383
Analyst RFE TNMHC (ppbv-C) 2539.8

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	165.7	1-HEXENE	30.8
C_3	150.0	2-ETHYL-1-BUTENE	20.7
ISOBUTANE	30.7	n-HEXANE	76.2
ISOBUTENE	191.6	2-METHYL-2-PENTENE	15.2
n-BUTANE	42.4	t-2-HEXENE	25.0
t-2-BUTENE	29.4	2,4-DIMETHYLPENTANE	17.6
C-2-BUTENE	23.7	ISOVALERALDEHYDE	19.2
ISOPENTANE	22.7	C_6 ALKENE	15.0
1-PENTENE	16.8	BENZENE	53.3
2-METHYL-1-BUTENE	26.7	ISOHEPTANE	16.4
ISOPRENE	43.2	2,2,4-TRIMETHYLPENTANE	21.8
1,1-DICHLOROETHYLENE	46.7	n-HEPTANE	26.4
C_5 ALKANE	30.1	C_7 ALKANE	11.4
C-2-PENTENE	27.7	METHYLCYCLOHEXANE	10.3
2-METHYL-2-BUTENE	18.3	2,5-DIMETHYLHEXANE	19.8
C_5 ALKENE	105.1	2,3,4-TRIMETHYLPENTANE	21.0
C_6 ALKANE	35.3	TOLUENE	94.1
CYCLOPENTENE	10.9	C_8 ALKANE	24.0
CYCLOPENTANE	13.5	3,5,5-TRIMETHYLHEXANE	15.2
ISOHEXANE	10.5	3-METHYLHEPTANE	18.5

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 42 Canister # 2

Sample Description LF-14 ON LF-1

Analysis Date 21 JANUARY 1983 Dilution Factor 0.2383

Analyst RFE TNMHC (ppbv-C) 2539.8

Compound	Concentration (ppbv-C)	Compound	Concentration
225-TRIMETHYLHEXANE	15.5	C_{10} ALKANE	13.8
1-OCTENE	10.2	1-DECENE	17.3
n-OCTANE	28.9	n-DECANE	29.9
C-2-OCTENE	15.8	123-TRIMETHYLBENZENE	25.6
CHLOROBENZENE	51.8	C_{11} ALKANE	15.0
ETHYLBENZENE	22.8	INDAN	10.4
m&p-XYLENE	63.7	C_{11} ALKENE	24.2
C_9 SATURATED ORGANIC	22.2	C_{11} ALKANE	10.7
C_9 ALKENE	13.2	m-DIETHYLBENZENE	35.8
STYRENE	23.2	C_{11} SATURATED ORGANIC	10.9
o-XYLENE	12.6	C_{11} ALKENE	27.5
1-NONENE	12.3	C_{11} ALKANE	22.1
C_{10} SATURATED ORGANIC	27.0	C_{11} SATURATED ORGANIC	14.0
C_{10} SATURATED ORGANIC	10.1	n-UNDECANE	25.6
C_{10} ALKENE	14.6		
m-ETHYLTOLUENE	24.1		
p-ETHYLTOLUENE	16.8		
135-TRIMETHYLBENZENE	53.2		
β-PINENE	10.7		
t-BUTYLBENZENE	38.8		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 43 Canister # 10
Sample Description 30 min. Sample from time box was tilled
Analysis Date 9 FEBRUARY 1983 Dilution Factor 0.4283
Analyst RFE TNMHC (ppbv-C) 1348.7

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	163.0	n-PROPYLBENZENE	14.8
C_3	24.1	p-CHLOROTOLUENE	13.7
ISOBUTANE	41.2	p-ETHYLTOLUENE	29.9
n-BUTANE	23.6	C_{10} ALKENE	60.0
ISOPENTANE	11.7	C_{10} ALKANE	17.2
ISOPRENE	21.6	t-BUTYLBENZENE	28.0
NEOHEXANE	10.3	1,2,4-TRIMETHYLBENZENE	13.4
2,3-DIMETHYLBUTANE	50.6	C_{10} AROMATIC	42.1
3-METHYLPENTANE	16.3	n-DECANE	62.2
1-HEXENE	16.7	C_{11} ALKANE	18.6
t-2-HEXENE	26.7	C_{11} ALKANE	26.3
BENZENE	11.8	C_{11} ALKANE	18.7
TRICHLOROETHYLENE	10.0	C_{11} ALKENE	45.6
2,5-DIMETHYLHEXANE	20.6	C_{11} ALKANE	19.8
TOLUENE	31.7	C_{11} ALKANE	18.9
CHLOROBENZENE	11.9	C_{11} ALKANE	11.1
m & p-XYLENE	20.2	C_{11} ALKANE	20.7
4-NONENE	14.4	C_{11} SATURATED ORGANICS	55.8
C_{10} ALKENE	11.7	C_{11} SATURATED ORGANIC	52.6
C_{10} ALKANE	14.8	n-UNDECANE	78.2

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 43 Canister # 10

Sample Description 30 MIN SAMPLE FROM TIME BOX WAS TILLED

Analysis Date 9 FEBRUARY 1983 Dilution Factor 0.4283

Analyst RFE TNMHC (ppbv-C) 1348.7

Compound	Concentration (ppbv-C)	Compound	Concentration
C_{11} AROMATIC	29.4		
C_{12} ALKANE	21.8		
C_{12} ALKANE	19.0		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 51 Canister # 68

Sample Description ——

Analysis Date 9 FEBRUARY 1983 Dilution Factor 0.4343

Analyst ZFE TNMHC (ppbv-C) 1832.1

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	31.5	2,2,5-TRIMETHYLHEXANE	14.4
C_3	25.5	n-OCTANE	10.6
ISOBUTANE	26.1	CHLOROBENZENE	41.1
ISOBUTENE	39.7	ETHYLBENZENE	12.0
1,3-BUTADIENE	21.5	m & p-XYLENE	45.5
n-BUTANE	31.9	STYRENE	26.4
t-2-BUTENE	29.3	4-NONENE	19.6
1-BUTYNE	17.4	C_{10} ALKANE	10.4
c-2-BUTENE	27.2	n-PROPYLBENZENE	39.2
ISOPENTANE	10.3	p-ETHYLTOLUENE	26.7
CYCLOPENTENE	12.7	1,3,5-TRIMETHYLBENZENE	56.6
3-METHYLPENTANE	16.6	t-BUTYLBENZENE	60.9
C_6 ALKANE	32.9	1,2,4-TRIMETHYLBENZENE	13.9
CHLOROFORM	60.4	C_{10} ALKANE	62.7
CARBON TETRACHLORIDE	18.3	ISOBUTYLBENZENE	42.7
CYCLOHEXENE	11.4	n-DECANE	20.8
TRICHLOROETHYLENE	10.7	C_{11} ALKENE	14.1
2,2,4-TRIMETHYLPENTANE	12.8	C_{11} ALKANE	30.4
2,3,4-TRIMETHYLPENTANE	11.9	C_{11} ALKANE	19.1
TOLUENE	64.0	m-DIETHYLBENZENE	19.3

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 51 Canister # 68
Sample Description —
Analysis Date 9-FEBRUARY 1983 Dilution Factor 0.4343
Analyst RFE TNMHC (ppbv-C) 1832.1

Compound	Concentration (ppbv-C)	Compound	Concentration
C_{10} UNSATURATED ORGANIC	13.3		
n-BUTYLBENZENE	20.9		
C_{11} ALKANE	12.0		
C_{11} ALKENE	41 3		
C_{11} ALKANE	58.5		
C_{11} SATURATED ORGANIC	15.5		
C_{11} AROMATIC	46.7		
C_{11} SATURATED ORGANIC	11 7		
1-UNDECENE	22.4		
n-UNDECANE	108 7		
C_{11} AROMATIC	26.3		
C_{12} ALKANE	25.0		
C_{12} ALKANE	40.4		
NAPHTHALENE	47.7		
ALKANE $>C_{12}$	36.6		

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 51 Canister # 16

Sample Description 30 MINUTE SAMPLE FROM TIME BOX WAS TILLED

Analysis Date 9 FEBRUARY 1983 Dilution Factor 0.4810

Analyst RFE TNMHC (ppbv-C) 8901.3

Compound	Concentration (ppbv-C)	Compound	Concentration
C_2	15.6	C_9 ALKANE	10.0
C_3	37.8	C_9 ALKANE	16.4
ISOBUTANE	14.8	ETHYLBENZENE	16.9
n-BUTANE	66.7	m&p-XYLENE	12.0
ISOPENTANE	24.8	C_9 SATURATED ORGANIC	35.3
n-PENTANE	31.0	STYRENE	45.8
1,1-DICHLOROETHYLENE	14.9	o-XYLENE	26.7
ISOHEXANE	13.3	C_{10} ALKANE	17.6
n-HEXANE	25.1	1-NONENE	14.5
2,2,4-TRIMETHYLPENTANE	28.4	n-NONANE	99.0
2,5-DIMETHYLHEXANE	15.4	ISOPROPYLBENZENE	15.9
2,3,4-TRIMETHYLHEXANE	21.3	C_{10} ALKANE	23.9
TOLUENE	33.0	C_{10} ALKENE	40.6
C_8 ALKANE	11.3	C_{10} ALKANE	18.9
3,5,5-TRIMETHYLHEXANE	16.4	C_{10} ALKANE	46.7
3-METHYLHEPTANE	18.8	C_{10} SATURATED ORGANIC	41.8
2,2,5-TRIMETHYLHEXANE	28.0	m-ETHYLTOLUENE	69.9
C_9 ALKANE	30.8	p-ETHYLTOLUENE	130.9
n-OCTANE	24.5	1,3,5-TRIMETHYLBENZENE	216.2
CHLOROBENZENE	23.5	C_{10} ALKANE	81.2

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 51 Canister # 16
Sample Description 30 MINUTE SAMPLE FROM TIME BOX WAS TILLED
Analysis Date 9 FEBRUARY 1983 Dilution Factor 0.4810
Analyst KEE TNMHC (ppbv-C) 8901.3

Compound	Concentration (ppbv-C)	Compound	Concentration
C_{10} ALKANE	16.6	C_{11} ALKENE	350.8
t-BUTYLBENZENE	85.2	C_{11} ALKENE	48.6
C_{10} ALKANE	71.9	C_{11} SATURATED ORGANIC	64.5
C_{10} ALKANE	22.0	C_{11} SATURATED ORGANIC	58.3
1-DECENE	52.0	C_{11} ALKENE	139.1
n-DECANE	456.4	1-UNDECENE	276.1
1,2,3-TRIMETHYLBENZENE	172.9	C_{11} AROMATIC	153.0
C_{11} SATURATED ORGANIC	43.6	n-UNDECANE	893.5
C_{11} ALKANE	98.6	C_{11} AROMATIC	246.9
C_{11} ALKANE	87.6	C_{11} ALKANE	52.7
C_{11} ALKANE	188.2	C_{11} ALKANE	26.0
C_{11} ALKENE	216.2	SATURATED ORGANIC ($>C_{11}$)	90.0
C_{11} ALKANE	160.7	AROMATIC ($>C_{11}$)	186.3
C_{11} ALKANE	368.6	ALKANE ($>C_{11}$)	70.1
n-BUTYLBENZENE	184.7	AROMATIC ($>C_{11}$)	312.3
C_{11} ALKENE	124.0	ALKENE ($>C_{11}$)	90.4
C_{11} ALKANE	137.0	ALKANE ($>C_{11}$)	36.6
C_{11} ALKENE	186.8	SATURATED ORGANIC ($>C_{11}$)	74.2
C_{11} SATURATED ORGANIC	165.1	ALKANE ($>C_{11}$)	43.7
C_{11} AROMATIC	350.8	AROMATIC ($>C_{11}$)	65.0

LANDFARM CRYOGENIC-GC ORGANIC SPECIES ANALYSIS

Run # 51 Canister # 16

Sample Description 30 MINUTE SAMPLE FROM TIME BOX WAS TILLED

Analysis Date 9-FEBRUARY 1983 Dilution Factor 0.4810

Analyst RFE TNMHC (ppbv-C) 8901.3

Compound	Concentration (ppbv-C)	Compound	Concentration
ALKANE ($>C_{11}$)	89.7		
ALKANE ($>C_{11}$)	65.1		
ALKANE ($>C_{11}$)	76.7		
NAPHTHALENE	104.4		
ALKANE ($>C_{11}$)	20.6		
ALKANE ($>C_{11}$)	14.9		
ALKANE ($>C_{11}$)	14.4		
ALKANE ($>C_{11}$)	153.2		
ALKANE ($>C_{11}$)	49.2		